İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

GRAFTING COPOLYMERIZATION OF ITACONIC ACID AND ITS DERIVATIVES ONTO POLYOLEFINES

M.Sc. Thesis by

Gülnur Başer

Department: Polymer Science and Technology

Programme: Polymer Science and Technology

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Advisor (Chairman) : Prof. Dr. Nurseli UYANIK (İ.T.Ü.)

Coadvisor : Prof. Dr. Candan ERBİL (İ.T.Ü.)

Members of the Examining Committee : Prof. Dr. Tuncer ERCİYES (İ.T.Ü.)

Prof. Dr. Hüseyin YILDIRIM (Y.T.Ü.)

Assoc. Dr. Seniha GÜNER (İ.T.Ü.)

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

İTAKONİK ASİT VE TÜREVLERİNİN POLİOLEFİNLER ÜZERİNE AŞI KOPOLİMERİZASYONU

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Gülnur Başer

515031016

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Tez Danışmanı : Prof. Dr. Nurseli UYANIK (İ.T.Ü.)

Tez Ortak Danışmanı : Prof. Dr. Candan ERBİL (İ.T.Ü.)

Diğer Jüri Üyeleri : Prof. Dr. Tuncer ERCİYES (İ.T.Ü.)

Prof. Dr. Hüseyin YILDIRIM (Y.T.Ü.)

Doç. Dr. Seniha GÜNER (İ.T.Ü.)

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September 2005 Gülnur BAŞER

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dΔQ/dt	: the change of added heat ΔQ with time
η	:viscosity number
υ	:velocity
γ	:rate of shear
σ	:shear stress
σ_0	:the yield stress,
η_0	:the viscosity at lower shear rates
η_∞	:at the higher shear rates
W	: the angular velocity of the cone and plate rheometer
θ	:cone angle
τ	:shear stress
T	:torque
r-component	
θ-component	
ϕ-component	: cylindirical coordinates

SUMMARY

GRAFTING COPOLYMERIZATION OF ITACONIC ACID AND ITS DERIVATIVES ONTO POLYOLEFINES

Polyolefins, such as polyethylene (PE, PP), are thermoplastics of high consumption because of their well balanced physical and mechanical properties, good moisture stability, and easy processability at a relatively low cost, which makes them a versatile material with continuously increasing applications. However, in some cases, not all the characteristics of these materials are suitable for common service conditions. So, one of their major drawbacks is their low impact strength, in particular, at low temperatures. Moreover, there is no polar group on the macromolecules of polyolefins, which makes its chemical reactions and compatibilizing with other polymers and process additives difficult, so the introduction of polar groups onto the main chains of polyolefins is method which is mostly used in recently years.

In recent years, many aspects of the grafting mechanisms of polar monomers such as maleic anhydride, glycidyl methacrylate, succinic acid, itaconic acid (IA), itaconic esters, with respect to polyolefin macro molecules have been investigated. Reactive extrusion and molten state reaction methods are often used.

In this work, grafting degree will be measured after grafting of IA and its monoesters onto low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and isotactic polypropylene (i-PP) by microwave irradiation, the effects of initiator concentration, monomer concentration and polymerization period to grafting efficiency of LDPE with IA will be examined and thermal and rheological properties of grafted polymers will be investigated.

All grafting reactions were carried out at 140°C with 100 W microwave input power. Polyolefin was dissolved in xylene then was mixed together with DBPO and monomer in a certain proportion. In all experiments, the weight ratio of xylene to polyolefins is always 10/1.

In grafting of LDPE with IA, influences of monomer content, initiator content and polymerization period on grafting degree were determined by pre-examinations. According to these results optimum reacion conditionswere determined as 2 g/100 g LDPE monomer content, as 0.75 g/100 g LDPE initiator content and as 10 minute polymerizatiom period. The grafting ratios (GR) of synthesised grafted polymers were measured back titration with ethanolic KOH solution and isopropanolic HCl solution. Solution of LDPE-g-IA sample in xylene was extracted with 0.005 N KOH solution and back titrated with 0.005 N HCl solution.

Optimization of reaction conditions that will be used for synthesis grafted LDPE, LLDPE and i-PP, which will be worked on their rheological and thermal properties, was determined in pre-examinations. Grafting of LDPE, LLDPE and i-PP with IA, monomethyl itaconate (MMI), monobutyl itaconate (MBI) and monooctyl itaconate (MOI) were provided in optimum conditions and results in Table 1 , 2 , 3 were obtained.

Table 1. Grafting Ratio of LDPE with IA and monoesters in optimum conditions and % conversions ([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power= 100 W)

Sample No.	Monomer	Monomer Concentration in Reaction Medium (mol /100 g LDPE)	% Grafting Ratio (mol /100 g LDPE)	% Grafting Ratio (g / 100 g LDPE)	% Conversion (g/100 g LDPE)
8	IA	0.01538 mol (2.0 g)	0.001115	0.145	7.25
17	MMI	0.01538 mol (2.2 g)	0.002232	0.321	14.52
18	MBI	0.01538 mol (2.9 g)	0.001997	0.371	12.98
19	MOI	0.01538 mol (3.7 g)	0.001674	0.405	10.88

Table 2. Grafting Ratio of LLDPE with IA and monoesters in optimum conditions and % conversions ([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power= 100 W)

Sample No.	Monomer	Monomer Concentration in Reaction Medium (mol /100 g LLDPE)	% Grafting Ratio (mol /100 g LLDPE)	% Grafting Ratio (g / 100 g LLDPE)	% Conversion (g/100 g LLDPE)
20	IA	0.01538 mol (2.0 g)	0.00058	0.0845	4.225
21	MMI	0.01538 mol (2.2 g)	0.001241	0.1728	7.854
22	MBI	0.01538 mol (2.9 g)	0.001185	0.2204	7.600
23	MOI	0.01538 mol (3.7 g)	0.000621	0.1503	4.03

Table 3. Grafting Ratio of i-PP with IA and monoesters in optimum conditions and % conversions ([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power= 100 W)

Sample No.	Monomer	Monomer Concentration in Reaction Medium (mol /100 g i-PP)	% Grafting Ratio (mol /100 g i-PP)	% Grafting Ratio (g / 100 g i-PP)	% Conversion (g/100 g i-PP)
24	IA	0.01538 mol (2.0 g)	0.001128	0.1466	7.332
25	MMI	0.01538 mol (2.2 g)	0.002107	0.3034	13.79
26	MBI	0.01538 mol (2.9 g)	0.0018853	0.3506	12.09
27	MOI	0.01538 mol (3.7 g)	0.0014417	0.3489	9.43

According to data in Table 1, 2 and 3 grafting efficiency of IA is lower than its monoesters because of its low reactivity. Grafting efficiency of monoesters decreases with increasing of chain length on ester group as compared with each other.

The monomer contents of itaconic acid and monoesters in reaction medium were arranged in such a way that the mole carboxyl groups/weight percent of grafting ratios

are nearly the same for a better comparison of thermal and rheological properties of LDPE, LLDPE and i-PP.

According to the rheological results, Shear rate-Viscosity, Shear stress-Viscosity, G' (Storage modulus)-Frequency, G''(Loss modulus)-Frequency, G'-G'' and Complex viscosity-frequency curves were plotted. It was shown that for LDPE at frequency values higher than 0.5 Hz G' and G'' values of ungrafted LDPE are higher than those of the grafted LDPEs, for LLDPE at frequency values lower than 15.78 Hz G' and G'' values of ungrafted LLDPE are lower thwn those of the grafted LLDPEs, at frequency values higher than 15.78 Hz G' and G'' values of all samples of LLDPE are equal each other, for i-PP at all frequency values, G' and G'' values of all i-PP samples are equal. The plot of log log G'-G'' for all polymers are very nearly linear.

Shear stress-Viscosity, Shear rate-Viscosity, Complex viscosity-Frequency curves showed that viscosity values of polymers change by grafting.

When Shear rate-Viscosity curves of grafted polymers were compared with each other it was shown that viscosity values of LDPE and LLDPE increase by grafting while viscosity values of i-PP decrease by grafting. (Figure 1, 2, 3)

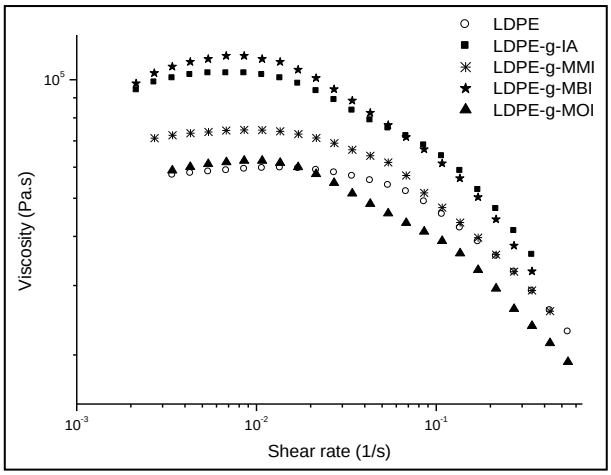


Figure 1. Shear rate-Viscosity curve of LDPE and grafted LDPEs

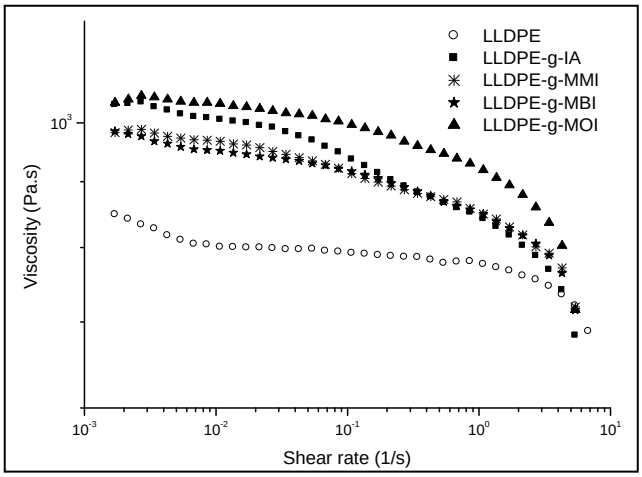


Figure 2. Shear rate-Viscosity curve of LLDPE and grafted LLDPEs

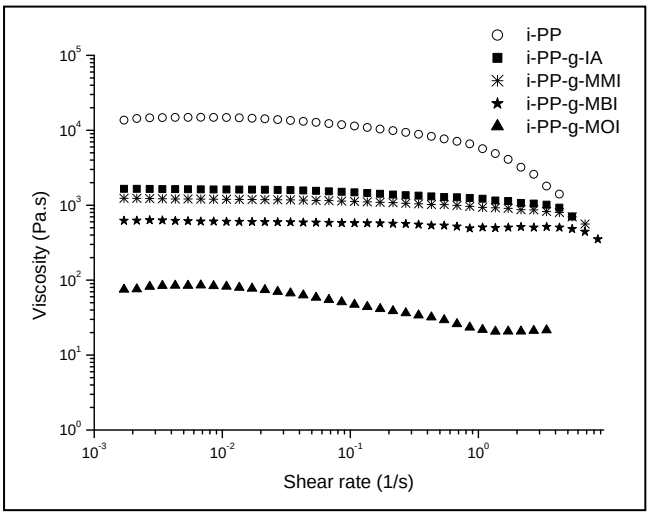


Figure 3. Shear rate-Viscosity curve of i-PP and grafted i-PPs

In addition, LDPE was grafted with MBI using three different monomer (IA) contents and predetermined optimization conditions to obtain LDPE-g-MBI samples. The monomer contents of itaconic acid in reaction medium were arranged in such a way that the mole carboxyl groups/weight percent of grafting ratios are sequential (from the lowest to the highest). Shear rate-Viscosity curve of samples shows that viscosity values of LDPE increase by grafting. (Figure 4.)

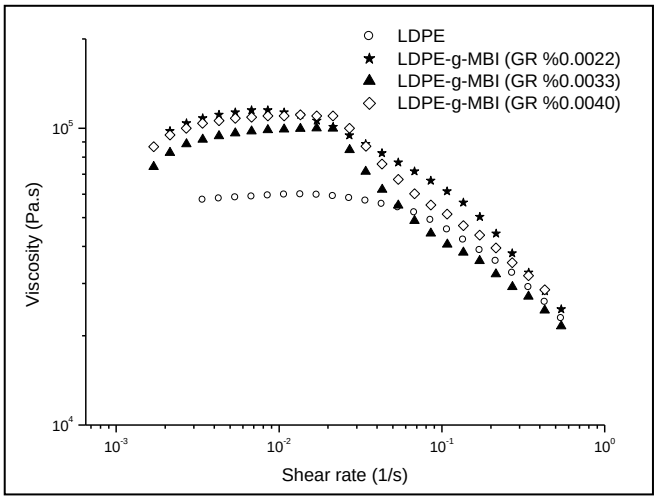


Figure 4. Shear rate-Viscosity curve of LDPE-g-MBI in a different grfating ratios

ÖZET

İTAKONİK ASİT VE TÜREVLERİNİN POLİOLEFİNLER ÜZERİNE AŞI KOPOLİMERİZASYONU

Poliolefinler (PE, PP vb.) fiziksel ve mekaniksel özelliklerinin iyiliği, nem tutmaması, düşük maliyetlerde kolay işlenebilirliği ve bir çok uygulamada çok yönlü materyal olarak kullanılabilmesinden dolayı çokça tüketilen termoplastik polimerlerdir. Fakat bazı durumlarda, olefinlerin bazı özellikleri kullanıma uygun değildir ve bu durum uygulama alanlarını kısıtlamaktadır. Bu özelliklerden en önemlisi, düşük sıcaklıklarda gösterdikleri düşük darbe dayanımlarıdır. Aynı zamanda poliolefin makromoleküllerinin üzerinde hiç polar grup bulunmaması onların kimyasal reaksiyonlarını ve diğer polimerlerle ve proses katkı maddeleriyle uyumlu biçimde karışmalarını zorlaştırdığından, nihai ürünün özelliklerini geliştirmek açısından, ana zincir üzerine polar grupların takılması son zamanlarda çokça ugulanan bir metoddur.

Bu amaçla, maleik anhidrit, glisidil metakrilat, süksinik asit, itakonik asit ve itakonik esterler gibi polar monomerlerin poliolefin makromolekülleri üzerine aşılanması birçok yöntemle çalışılmıştır. Reaktif ekstrüzyonda ve eriyik ortamda aşı kopolimerizasyonu bunlar arasında sıkça kullanılanlardır.

Bu çalışmada, itakonik asit (IA) ve itakonik asidin mono esterlerinin alçak yoğunluklu polietilen(AYPE), lineer alçak yoğunluklu polietilen (LAYPE) ve izotaktik polipropilen (i-PP) üzerine, mikrodalga sistemi yardımıyla aşılanması sonucu aşılanma dereceleri ölçüldü, AYPE'nin itakonik asit ile aşılanmasında aşılanma derecesi üzerine başlatıcı ve monomer konsantrasyonu, polimerizasyon periyodu gibi parametlerin etkisi incelendi, son olarak da aşılanmış polimerlerin reolojik ve termal özelliklerinde değişiklik olup olmadığı gözlendi.

Aşılanmış poliolefinler 1gr polimer/10 gr çözücü oranında ksilen çözücüsü içinde, 140^0C sıcaklıkta, 100 W gücündeki mikro dalga boyunda, başlatıcı olarak dibenzoil peroxit (DBPO) kullanılarak sentezlendi.

AYPE'nin itakonik asit ile aşılanmasında aşılanma derecesi üzerine başlatıcı ve monomer konsantrasyonu, polimerizasyon periyodu gibi parametlerin etkisini belirlemek üzere ön çalışmalar yapıldı. Elde edilen sonuçlar değerlendirilerek optimum reaksiyon koşulları; başlatıcı konsantrasyonu 0.75 g/100 g AYPE, monomer konsantrasyonu 2 g/100 g AYPE ve polimerizasyon periyodu 10 dakika olarak belirlenmiştir. Aşılama periyodu sonucunda elde edilen aşı kopolimerlerin aşılanma dereceleri etanolik potasyum hidroksit (KOH) ve izopropanolik hidroklorik(HCl) asit çözeltileriyle geri titrasyon yapılarak analiz edilmiştir.Bu amaçla IA-g-LDPE örneğinin ksilendeki çözeltisi 0.005 N etanolik KOH çözeltisiyle ekstrakte edilerek 0.005 N izopropanolik HCl çözeltisiyle geri titre edilmiştir.

Aşılanmış AYPE, LAYPE ve i-PP'nin termal ve reolojik özelliklerinin incelenmesinde üzerinde çalışılacak olan örneklerin sentezlenmesinde ön çalışmalarda belirlenmiş olan optimum reaksiyon koşulları kullanıldı. AYPE, LAYPE ve i-PP'nin IA, monometil itakonat (MMI), monobütil itakonat (MBI) ve monooktil itakonat (MOI) ile aşılanması sonucu Tablo 1 , 2 , 3' teki sonuçlar elde edilmiştir.

Tablo 1. AYPE'in optimum koşullarda IA ve monoesterlerle aşılanma dereceleri ve % dönüşümleri ([DBPO]= 0.75 g /100 g AYPE, T=140^0C, MW power= 100 W)

Örnek No.	Monomer	Reaksiyon Ortamındaki Monomer Konsantrasyonu (mol /100 g AYPE)	Aşılanma Derecesi % (mol /100 g AYPE)	Aşılanma Derecesi % (g / 100 g AY PE)	% Dönüşüm (g/100 g AYPE)
8	IA	0.01538 mol (2.0 g)	0.001115	0.145	7.25
17	MMI	0.01538 mol (2.2 g)	0.002232	0.321	14.52
18	MBI	0.01538 mol (2.9 g)	0.001997	0.371	12.98
19	MOI	0.01538 mol (3.7 g)	0.001674	0.405	10.88

Tablo 2. LAYPE'in optimum koşullarda IA ve monoesterlerle aşılanma dereceleri ve % dönüşümleri ([DBPO]= 0.75 g /100 g AYPE, T=140^{0}C, MW power= 100 W)

Örnek No.	Monomer	Reaksiyon Ortamındaki Monomer Konsantrasyonu (mol /100 g LAYPE)	Aşılanma Derecesi % (mol /100 gLAYPE)	Aşılanma Derecesi % (g / 100 g LAYPE)	% Dönüşüm (g/100 g LAYPE)
20	IA	0.01538 mol (2.0 g)	0.00058	0.0845	4.225
21	MMI	0.01538 mol (2.2 g)	0.001241	0.1728	7.854
22	MBI	0.01538 mol (2.9 g)	0.001185	0.2204	7.600
23	MOI	0.01538 mol (3.7 g)	0.000621	0.1503	4.03

Tablo 3. i-PP'in optimum koşullarda IA ve monoesterlerle aşılanma dereceleri ve % dönüşümleri ([DBPO]= 0.75 g /100 g i-PP, T=140^{0}C, MW power= 100 W)

Örnek No.	Monomer	Reaksiyon Ortamındaki Monomer Konsantrasyonu (mol /100 g i-PP)	Aşılanma Derecesi % (mol /100 g i-PP)	Aşılanma Derecesi % (g / 100 g i-PP)	% Dönüşüm (g/100 g i-PP)
24	IA	0.01538 mol (2.0 g)	0.001128	0.1466	7.332
25	MMI	0.01538 mol (2.2 g)	0.002107	0.3034	13.79
26	MBI	0.01538 mol (2.9 g)	0.0018853	0.3506	12.09
27	MOI	0.01538 mol (3.7 g)	0.0014417	0.3489	9.43

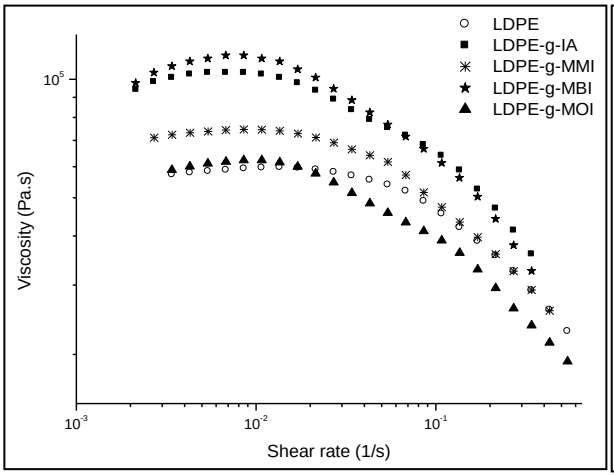
Tablo 1 , 2 ve 3' teki verilere göre IA'in aşılanma derecesi reaktiflik oranı düşük olduğundan beklenildiği gibi monoesterlerine göre daha düşük çıkmıştır. Esterlerde ise ester grubunun zincir uzunluğu arttıkça reaksiyona girme eğilimi azalmakta ve aşılanma derecesi düşmektedir.

AYPE, LAYPE ve i-PP'nin termal ve reolojik özelliklerinin incelenmesi esnasında iyi bir karşılaştırma sağlamak için, incelenecek örneklerin sentezi sırasında reaksiyon ortamındaki itakonik asit ve mono esterlerin monomer konsantrasyonu aşılanmış örneklerin " % mol karboksil grubu/ağırlık" aşılanma derecesi oranı birbirine yakın çıkacak şekilde ayarlanmıştır.

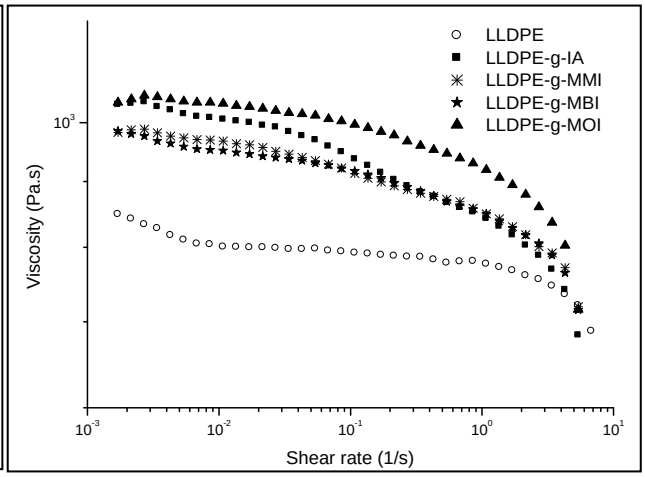
Yapılan reolojik çalışmalarda örneklerin Shear rate-Viskozite, Shear stress-Viskozite, G' (Elastisite modülü)- Frekans, G'' (Kayıp modülü)-rekans, G'-G'', Kompleks viskozite-Frekans grafikleri çizilmiş ve değerlendirilmiştir.

AYPE için 0.5 Hz'den yüksek frekanslarda aşılanmamış polimerin G' ve G'' değerlerinin aşılanmış polimerlerinkilerden yüksek olduğu, LAYPE için 15.78 Hz'den düşük frekanslarda aşılanmamış polimerin G' ve G'' değerlerinin aşılanmış polimerlerinkilerden daha düşük, 15.78 Hz'den yüksek frekanslarda ise aşılanmamış ve aşılanmış polimerlerin G' ve G'' değerlerinin eşit olduğu, i-PP için ise aşılanmamış ve aşılanmış tüm polimerlerin G' ve G'' değerlerinin tüm frekanslarda birbirine eşit olduğu gözlenmiştir. AYPE, LAYPE ve i-PP' in G'-G'' grafikleri doğrusala yakın çıkmıştır.

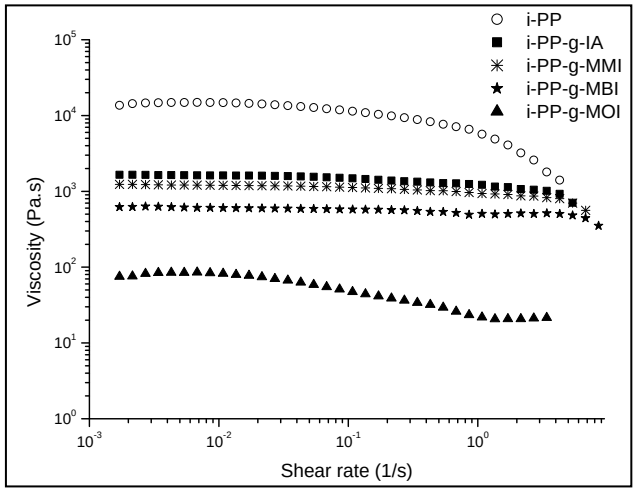
Shear stress-Viskozite, Shear rate-Viskozite ve Kompleks viskozite-Frekans grafikleri incelendiğinde aşılanmayla birlikte polimerlerin viskozitelerinin değiştiği gözlenebilmektedir.



Şekil 1. AYPE ve aşılanmış AYPE'lerin Shear rate-Viskozite grafiği



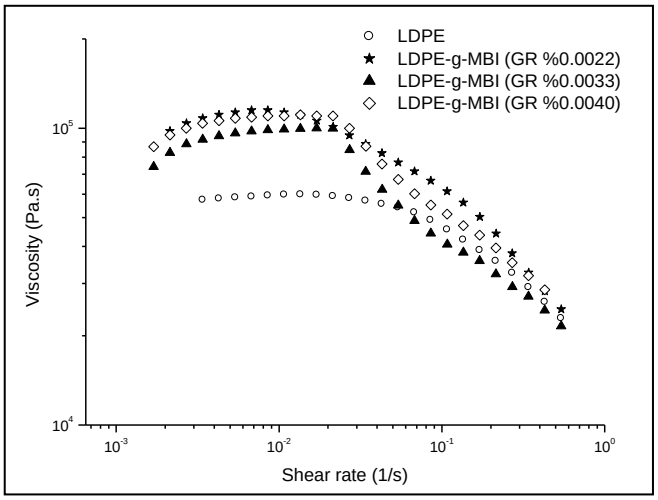
Şekil 2. LAYPE ve aşılanmış LAYPE'lerin Shear rate-Viskozite grafiği



Şekil 3. i-PP ve aşılanmış i-PP' lerin Shear rate-Viskozite grafiği

AYPE, LAYPE ve i-PP'in Shear rate-Viskozite grafikleri birbiriyle karşılaştırıldığında (Şekil 1, 2, 3) AYPE' in ve LAYPE' in viskozite değerlerinin aşılanmayla birlikte arttığı, i-PP' in viskozite değerlerinin ise aşılanmayla birlikte azaldığı gözlenmiştir.

Ek olarak AYPE, daha önceden belirlenmiş optimizasyon koşullarını da kullanarak MBI ile düşük bir değerden yüksek bir değere doğru üç farklı aşılınma derecesiyle aşılanmıştır. Bu örneklerin Shear rate-Viskozite grafiğinde de aşılanmamış AYPE'in viskozitesinin aşılanmayla birlikte arttığı gözlenmektedir. (Şekil 4.)



Şekil 4. AYPE ve MBI ile farklı aşılanma derecelerinde aşılanmış AYPE'lerin Shear rate-Viskozite grafiği

PART 1.

1.INTRODUCTION

Polyolefines, such as polyethylene (PE), polypropylene (PP), are thermoplastics of high consumption because of their well balanced physical and mechanical properties, good moisture stability, and easy processability at a relatively low cost, which makes them a versatile material with continuously increasing applications. However, in some cases, not all the characteristics of these materials are suitable for common service conditions. So, one of their major drawbacks is their low impact strength, in particular, at low temperatures. Moreover, there is no polar group on the macromolecules of polyolefines, which makes its chemical reactions difficult, so the introduction of polar groups onto the main chains of polyolefines is an important route.

Functionalization of polyolefines through grafting of polar monomers has been the subject of intense research during recent years with the aim of introduction functional polar groups into their non-polar olefinic chains. The resulting compounds have been used as compatibilizers in blends of polyolefines with other polar polymers. Several studies have shown that it is possible to compatibilize polyolefines by blending with a large number of polar polymers in order to improve properties of the final products.

In recent years, many aspects of the grafting mechanisms of some polar groups containing monomers with respect to polyolefin macromolecules have been investigated. Reactive extrusion and molten state reaction methods are often used.

However, there has not been a report on the solution grafting of itaconic acid or its monoesters onto polyolefines by microwave irradiation.

In this work, itaconic acid and its monoesters (monomethyl itaconate, monobutyl itaconate, monooctyl itaconate) were grafted onto polyethylenes and polypropylene in xylene solvents by microwave (MW) irradiation system in the presence of dibenzoyl peroxide as an initiator. MW irradiation method is a low temperature method. Its temperature is lower than that of melt grafting method and also the reaction period is very short as compared with other grafting methods. In this study, the effects of grafting on rheological and thermal properties of polyolefines were investigated.

PART 2.

2.THEORY

2.1. Polyolefins

The class of materials formed by the polymerization of certain unsaturated hydrocarbons is known as ‘olefines’ is an extremely important one. The main members are low density polyethylene (LDPE) and high density polyethylene (HDPE) and polypropylene (PP) together with some copolymers. [1-3] They are conveniently studied under one chapter heading since, on the whole, they form a family of polymers with a particular range of properties. Technically, polyisobutylene and polyisoprene are also polyolefines, but their properties render them more suitable for study in the chapter on synthetic rubbers. Common usage made the term ‘polyolefines’ synonymous with the polymers and copolymers of ethylene and propylene.

2.1.1. Polyethylenes

2.1.1.1. Classification of polyethylenes

Since one of the basic differences in the two polyethylenes is their densities they are often referred to as low-density and high-density polyethylenes. Another system of nomenclature is derived from the fact that the manufacturing conditions are very different, in particular, one is made under conditions of high pressure (15,000-30,000 lb/in^2), while the other uses pressures which are normally below 500 lb/in^2. The terms 'linear' and 'branched' polyethylene may also be encountered and these refer to the structure of the polymer molecules. The high-density polyethylene (produced by

the low-pressure process, contains less than one side chain per 200 carbon atoms in the main chain) is the linear type while the low-density (high-pressure) polyethylene possesses the branched molecule.

Examples of branching in a low-density polyethylene molecule are shown below (Figure 2.1)

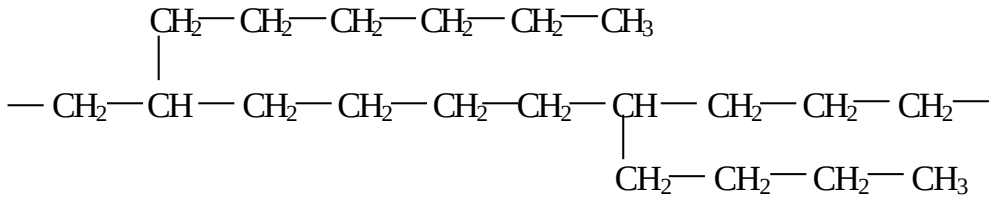


Figure 2.1. Branching in a low-density polyethylene molecule

Different grades of PE are the linear low density polyethylenes (LLDPE) which do not have long branches (linear alkenes that are shorter than those of LDPE). Their density is kept in the low range (0.880-0.925 g/cm^3) by the deliberate introduction of a controlled amount of short branches of the desired length. The molecules of LDPE, HDPE and LLDPE are represented schematically in Figure 2.2.

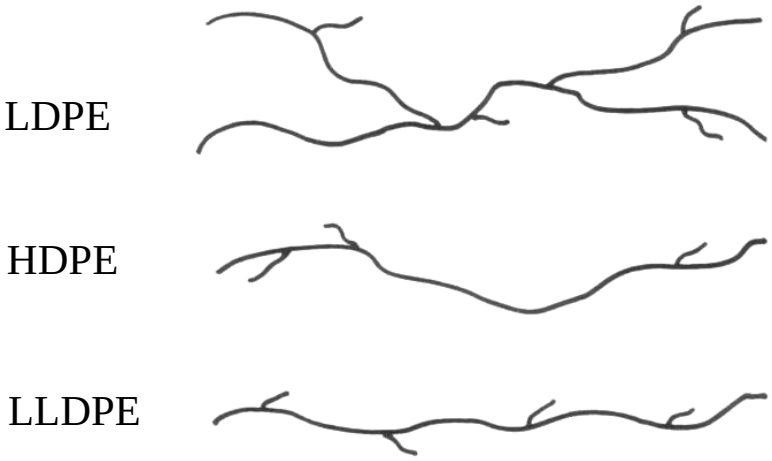


Figure 2.2. Molecules of LDPE, LLDPE and HDPE

Very low density polyethylene (VLDPE) ranges in density from 0.880 and 0.912 g/cm^3. Their low degree of crystallinity imparts outstanding low temperature impact properties, flexibility and increased permeability to gases. These characteristics made them suitable materials for geomembranes, agricultural film, packaging for fresh produce and impact modifiers.

High molecular weight (HMW-HDPE) and ultrahigh molecular weight (UHMW-PE) polyethylenes are both HDPE with MW in the range 300,000-500,000 and 3-6 millions respectively. HMW-HDPE has bimodal molecular weight dispersity, the very high MW fractions impart strength and toughness while the low MW fractions facilitate extrusion. UHMW-PE is used to produce extended chain fibers (ECPE), the highest modulus and highest strength fibers ever made.

2.1.1.2. Properties of polyethylenes

The main structural factors that determine PE properties are the degree of short and of long chain branching, the average MW and the polydispersity.

One of the most important characteristics that determine in the highest degree the properties and the behavior of different grades of PE is their branching. Branches prevent the polymer chains from packing together regularly and closely and have a predominant effect on the density of PE. The density can be considered a first indication of the degree of branching: the lower the density the higher the degree of branching. The effect of density on some general properties of PE is illustrated in Figure 2.3. The presence of branches interferes with the ability of the polymer to crystallize. The degree of crystallinity of LDPE is usually of the order of 55-70% compared with that of HDPE which is 75-90%.

Other properties depending on crystallinity, such as stiffness, hardness, tear strength, yield point, Young's modulus in tension and chemical resistance, increase with increasing degree of crystallinity (HDPE) whereas permeability to liquids and gases, flexibility and toughness decrease under the same conditions

Since PE is crystalline non-polar hydrocarbon polymer it has no solvents at room temperature and dissolution takes place only on heating in solvents of similar solubility parameter such as hydrocarbons and halogenated hydrocarbons. The higher the degree of crystallinity results the higher the dissolution temperature. LDPE dissolves at 60°C compared to 80-90°C for high density, more crystalline polymers.

The effect of branching also depends on the size of side chain branches. While short branches have a predominant influence on the degree of crystallinity and therefore on the density of the polymer, long branches affect more pronouncedly the polydispersity. The side chains may be as long as the main chain and like it may have

a wide distribution of lengths. The higher the MW of the resulting polymer the wider the MWD, as chain transfer reactions may occur as well on side chains.

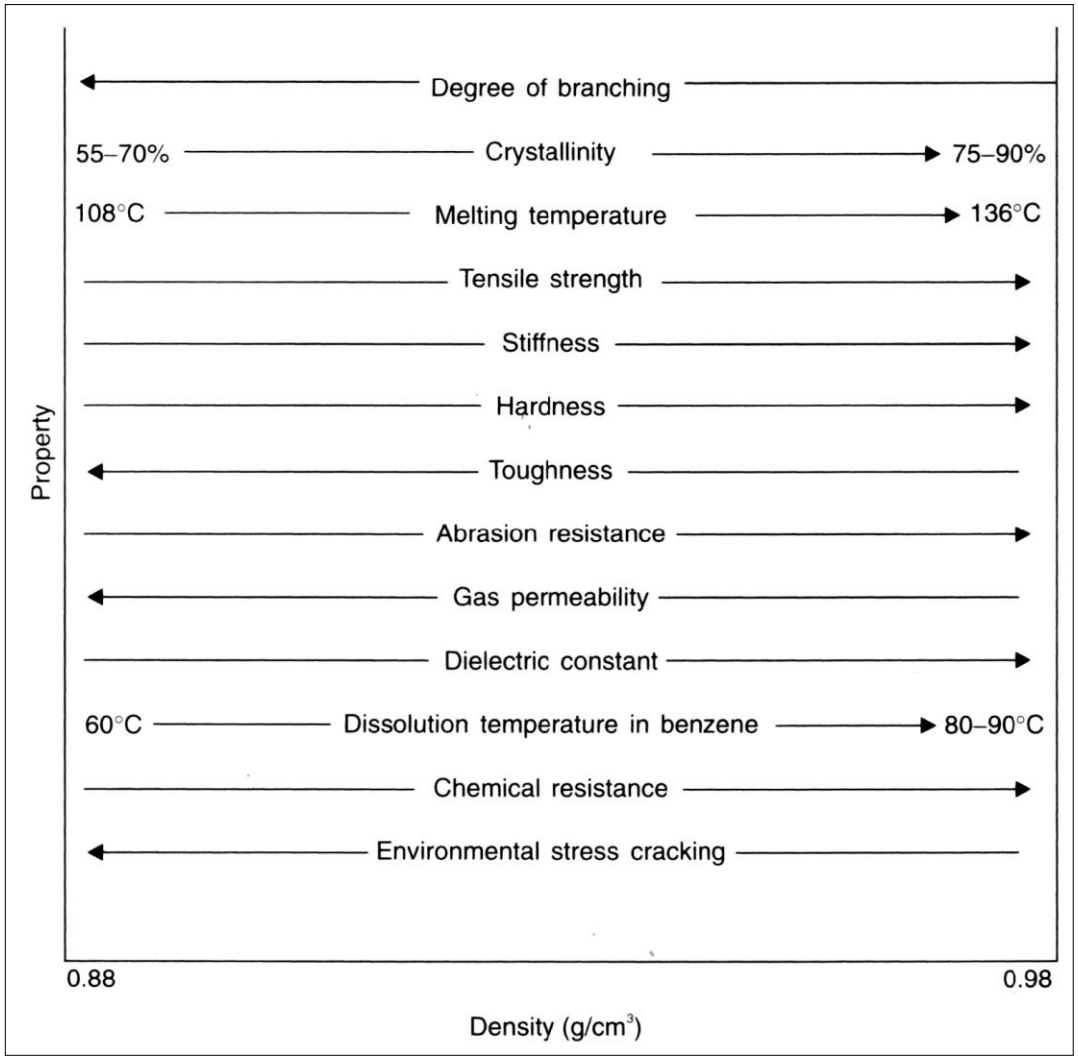


Figure 2.3. Effect of density on polyethylene properties

Such a polymer may be made up of short chains grafted onto short chains, long chains onto long chains and a vast range of intermediate cases.

Long chain branches also affect the flow properties. Long branched molecules are more compact and tend to entangle less with other molecules resulting in lower solution and melt viscosities as compared with unbranched polymers.

Another factor that influences the properties of the melt, as well as those properties that involve large deformations, is the weight-average MW. Ultimate tensile strength, tear strength, low temperature toughness, softening temperature, impact strength and

environmental stress cracking increase as the MW increases; on the contrary, the fluidity of the melt and the coefficient of friction (film) decrease.

For technological purposes, the MW is characterized by the melt flow index (MFI) that is the weight in grams extruded under a standard load in a standard plastometer at 190°C in 10 minutes. The higher is the MFI, the lower is the MW. However, MFI has to be considered carefully as the viscosity of the melt is strongly affected by the presence of long chain branches as has already been mentioned.

The influence of the density on some properties of different grades of PEs is illustrated in Table 2.1.

Table 2.1. Some properties of different grades of polyethylenes

Property	*LLDPE*	*LDPE*	*HDPE*	*UHMW-PE*	*Poly-methylene*
Density (g/cm^3)	0.910–0.925	0.915–0.935	0.941–0.967	0.93	0.98
Melting temperature (°C)	125	106–112	130–133	132	136
Tensile strength (MPa)	14–21	6.9–17.2	18–30	20–41	34.5
Elongation at break (%)	200–1200	100–700	100–1000	300	500
Flexural modulus (MPa)	248–365	415–795	689–1654	–	–
Izod impact strength (J/m)	–	0.67–21	27–160	no break	–
Hardness (Shore D)	41–53	45–60	60–70	–	–

The electrical insulating properties of polyethylenes are excellent. The dielectric constant increases linearly with increasing density. As it is a non-polar material, dielectric constant and the power factor are almost independent of temperature and frequency.

2.1.1.3. Application fields of polyethylenes

The widespread use of PE is due to its excellent electrical insulation properties and chemical resistance, easy processability and low cost.

The major applications of LDPE, LLDPE and HDPE have been as film for general packaging (bags, sacks, food wrapping) and building and agricultural industries. HDPE film has also been used in a net-like form (or pseudofiber).

PE, especially HDPE is an important injection molding material for a wide range of products including toys, electrical fittings, seals, chemical plants, containers, cases, crates, house wares and many other applications. Specialized uses include the disposable syringes for medical purposes. HDPE has been widely used for blow molding of bottles for milk and other foodstuffs, household chemicals and drug packaging. Squeeze bottles are made from LDPE.

Other areas for PE applications have been domestic water and gas piping, and agricultural piping. PE has also been used as filament for ropes, fishing nets and fabrics.

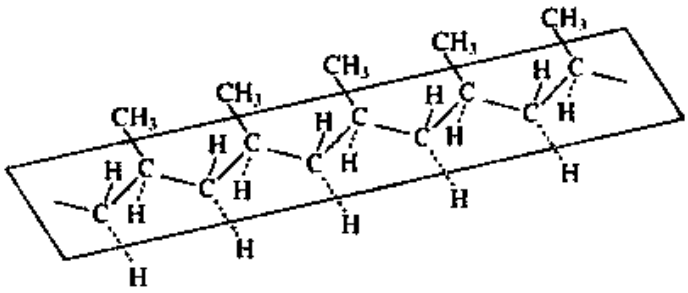
Based on its excellent electrical insulation properties, PE has been extensively used in cable and wire covering (undersea cables) and air-borne radar.

2.1.2. Polypropylenes

PP is a major volume thermoplastic material ranked third in the production of plastics, after PE and PVC. [1-3] Due to its cost effectiveness, versatility, overall competitiveness and excellent environmental aspects, PP is the fastest growing commodity plastic. Advanced polymerization processes in conjunction with highly developed compounding techniques make it possible to target PP for engineering applications.

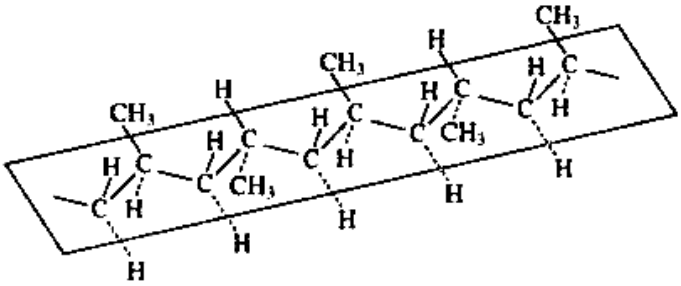
PP is produced by the stereospecific addition polymerization of propylene. The common name of the polymer is polypropyIene, which corresponds fairly well with the name recommended by IUPAC where the repeating propylene unit is in brackets. Using heterogeneous stereospecific catalysts, Natta in Italy obtained in 1954 crystalline polymers of propylene. Earlier efforts to polymerize propyIene had only resulted in amorphous polymers without any use at that time. Moreover, amorphous PP can be used for some special applications. [4-5] Natta classified the three geometric forms adopted by the polymer chain of PP as follows (Figure 2.4.) Isotactic and syndiotactic PPs are crystalline, whereas atactic polymer is amorphous.

a)



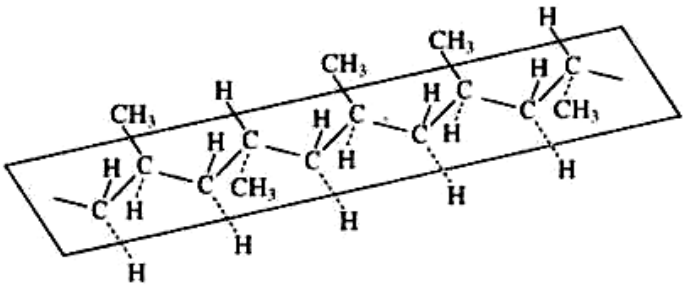
I.Isotactic: all methyl groups are situated on the same side of the chain

b)



II.Syndiotactic; methyl groups are on alternating sides

c)



III.Atactic; methyl groups are situated at random

Figure 2.4. Three geometric forms of polypropylene (a, b, c)

2.1.2.1. Properties of polypropylenes

PP is a crystalline polymer and the rate and manner in which the crystals have been formed from the melt influence the crystalline structure. This in turn largely determines both physical properties and processing characteristics of the polymer. Nucleation agents (crystalline organic acids or metal salts) are added in amounts below 0.1% to provide additional crystallization sites and the formation of smaller and more numerous polymer crystals. This controlled morphology of the polymer referred to as high crystallinity PP' results in higher bulk properties of the material,

namely the softening point, the stiffness, the tensile strength, the modulus and the hardness.

The melting temperature, Tm, of isotactic PP is 176°C, some 40°C higher than that of HDPE and this fact makes possible steam sterilization of many PP articles. Strain-free articles retain their shape even at 135-140°C. The glass transition temperature, Tg, of PP is situated at about 0°C and below this temperature the impact strength drops down and the polymer becomes brittle.

Some properties of PP:

density (g/cm^3) = 0.903; tensile strength (MPa) = 35.5;

tensile modulus (MPa) = 1380; flexural modulus (MPa) = 1690.

The non-polar nature of PP provides the material with excellent electrical properties similar to those of HDPE. Chemical resistance to most chemicals and solvents is exceptionally high. The polymer is insoluble at room temperature and dissolves in hydrocarbons and chlorinated hydrocarbons only above 80°C. Unlike PE, PP does not suffer environmental stress cracking.

PP differs from PE by the presence of methyl side branches and of relatively labile tertiary hydrogen atoms at every second carbon atom on the backbone. This makes the polymer more susceptible to oxidation by oxidizing agents and by air at elevated temperatures.

Processing methods such as injection molding, blow molding, fiber extrusion and film manufacture are the general processing techniques used with PP.

2.1.2.2. Application fields of polypropylenes

Around 30% of PP and its related copolymers is used as fibers and filaments produced by extrusion. Excellent wear and resistance to staining associated with low cost have led to uses in woven and non-woven form for carpeting in indoor and outdoor constructions, for clothing, inner liners, drapes, tea bags, wall coverings, furniture and automotive upholstery, and for ropes and netting. Another large market for PP and for its copolymers is as film (both oriented and cast) for packaging of food and tobacco products and for textile goods.

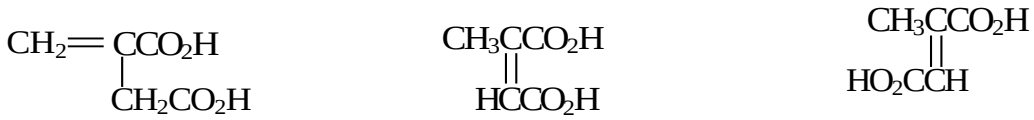
Atactic PP, which was an unwanted by-product for many years, is now specially produced for some applications. The material, which is intermediate between a wax and a rubber, is compatible with mineral fillers and bitumens. It has found use for roofing materials, as asphalt additive, for formulation of sealing and adhesive compounds and for paper laminating. [1,4-5]

Syndiotactic PP, which is not yet commercially available, has lower Tm, better impact resistance and more clarity than isotactic PP.

An obvious advantage of PP is its ease of recycling; this is especially important in many of the packaging and automotive applications.

2.2. Itaconic Acid and Itaconic Esters

Itaconic acid, 2-methylenesuccinic acid (I) was isolated from the pyrolysis products of citric acid and characterized by Baup in 1836. [6] Itaconic acid and the isomeric citraconic (II) and mesaconic (III) acids (Figure 2.5) may be converted to each under certain conditions.



(I) (II) (III)

Figure 2.5. Isomers of itaconic acid: Itaconic acid (I) Citraconic acid (II) and mesaconic (III) acid.

Itaconic acid is produced commercially by fermentation of carbonhydrates by Aspergillus terreus (Figure 2.6). Glucose or row cane or corn sugar may be used as the carbon source, but molasses is preferred because of the low cost.

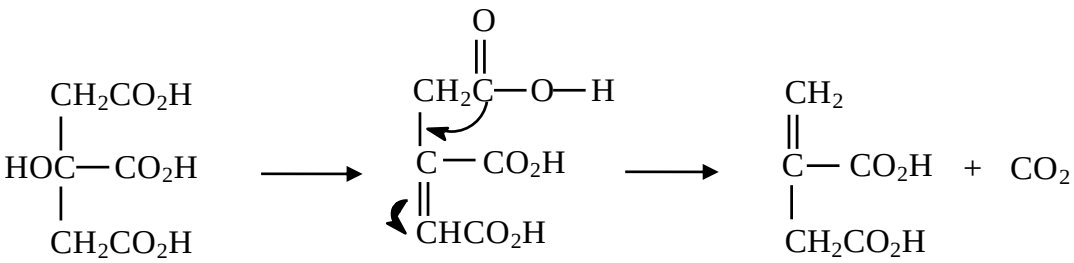


Figure 2.6. Production of itaconic acid via decarboxylation

Other syntheses of itaconic acid include the classical pyrolysis of citric or aconitic acids.

Fischer esterification of itaconic acid is a satisfactory route to simple dialkyl esters. Commercial quantities of dimethyl and di-n-butyl itaconate are made in this way. Monoester prepared by direct esterification of the acid may be freed of diester by extraction with aqueous sodium bicarbonate and reacidification.

Itaconic acid has been used more extensively in industry than any of its monomeric derivatives. Copolymerization with other monomers during the manufacture of synthetic latexes results in improved emulsion stability to freezing and thawing and to mechanical shear, as well as increased adhesion of the polymer upon application to various substrates. Incorporation of small amounts in polymeric acrylonitrile fibers improves dye receptivity. Water-soluble copolymers of the acid with acrylamide or acrylic acid are never materials that are being examined in textile and related application. Di-n-butyl itaconate has been used as an internal plasticizer in vinyl acetate paint latexes. A great variety of polymers incorporating the itaconates has been reported in the patent literature, but many of these have not been produced commercially.

Itaconic compounds are relatively innocuous materials which can be handled without special precautions. Oral toxicities of the acid and its monomethyl and monobutyl esters are low. Itaconic acid and di-n-butyl itaconate are acceptable components of food packaging materials when used in minor amounts. Polyethylene and semirigid or rigid vinyl and acrylic resins incorporating itaconic acid in polymerized form have also been the subjects of Food Additive Regulations.

Itaconic acid and its derivatives have been the subject of intense research, which is especially on their polymerization reaction reactivities, degradation and thermal and solubility properties, during recent years. It has been reported in the literature that itaconic acid does not homopolymerize, although it has been found to enter into copolymerization reactions in numerous instances. Since itaconic esters do homopolyerize to materials of fairly high molecular weight, the failure to bring about polymerization of the acid appeared to be anomalous.

For the first time, polymerization reactions of itaconic acid and its derivatives were studied in 1959. Itaconic acid was underwent homopolymerization in solution hydrochloric acid using persulfate initiation.[7]

In another work, dialkyl itaconates were homopolymerized easily to give vinylidene-type polymers having molecular weights of 7,000-110,000.[8]

In a study being on the synthesis and characterization of poly (itaconate ester)s with short poly(ethylene oxide) side chains, it was found that the monomer syntheses via esterification of itaconic acid resulted in incomplete esterification leaving up to 35 mol% monomers with carboxylic acid functionality.[9]

Gargallo and his coworkers made several studies about synthesis, characterization, Dielectric properties, viscoelastic relaxations of IA and its esters.[10-13]

Studies about viscosity, thermal and transition properties of itaconic esters are another studies which have been made for 20 years.[14-16]

Block copolymers of itaconates have been synthesized and made investigations on their thermal degradation many times. [17-20]

2.3. Types of Copolymers

A and B monomers which have different chemical structure can give several different types copolymers according to their sequential arrangements. Here A, implies monomer one and B implies monomer two.

Copolymers containing two monomer structures that are randomly distributed can be termed random copolymers (2.1):

—AABBBABABBAABA— **(2.1)**

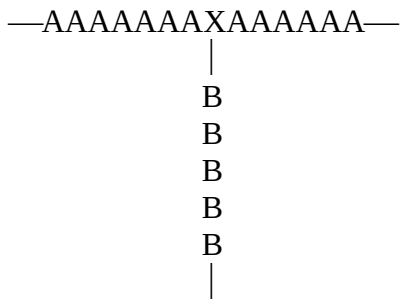
Equimolar compositions with a regularly alternating distribution of monomer units are alternating copolymers (2.2):

—ABABABABABABAB— **(2.2)**

A linear copolymer that contains one or more long uninterrupted sequences of each of the comonomer species is a block copolymer (2.3):

—AAAAAA-BBBBBBB— **(2.3)**

A graft copolymer is a polymer comprising molecules with one or more species of block connected to the main chain as side chains, having constitutional or configurational features that differ from those in the main chain, exclusive of branch points. The simplest case of a graft copolymer can be represented by structure (2.4)



(2.4)

where a sequence of A monomer units is referred to as the main chain or backbone, the sequence of B units is the side chain or graft, and X is the unit in the back bone to which the graft is attached .In graft copolymers the backbone and side chains may both be homopolymeric, the backbone may be homopolymeric and the side chains copolymeric or vice versa, or both backbone and side chains may be copolymeric but

of different chemical compositions. Branching in one or more stages and cross-linking may also occur.

2.4. Synthesis Methods of Graft Copolymers

Free-radical polymerization methods are the oldest and most widely used procedures for the synthesis of graft polymers, because they are relatively simple. However, they usually give heterogeneous materials that are difficult to characterize. More recent methods have been developed to produce graft polymers with relatively well-defined structures.[1]

2.4.1. Grafting by free radical initiation

Radical polymerization is usually initiated by peroxidic compounds which are homolytically cleaved at their O—O bond. The resulting radicals react with monomers and start the growth of macroradicals. If the peroxy group is attached to a macromolecular chain then its decomposition can be used for direct activation of a polymer. Introduction of peroxy groups can be effected in various ways, e.g. reaction of a pendant acyl chloride with tert-butyl hydroperoxide (Figure 2.7).

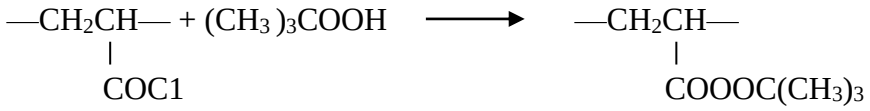


Figure 2.7. Presentation of a macromolecular initiating

The macroradicals formed by thermal decomposition of such polymer peroxide initiate grafting, while the tert-butoxy radicals also produced start ordinary homopolymerization. Although the efficiency of grafting for a macromolecular initiator is higher than those achieved with a low-molecular peroxide, monomer and polymer system.

Many different methods have been attempted to achieve the direct chemical generation of radicals in macromolecules of different structures but these have been confined to the laboratory scale.

2.4.2. Radiation grafting

The effort devoted to the optimization of grafting and to improving its efficiency led to the use of ionizing radiation which is particularly suitable for the less reactive saturated thermoplasts. Even though irradiation of a mixture of macromolecules and polymerizable monomer also produces unwanted homopolymer, the efficiency of grafting may be enhanced by a careful choice of monomer and polymer. The most efficient grafting involves monomers which give a low radiation yield of radicals as compared with the grafted polymer. When poly (vinyl chloride) swollen with styrene is irradiated grafting occurs with an efficiency of almost unity. [21]

If the polymer needs to be grafted with a monomer giving a high radiation yield of free radicals; the monomer is best supplied as a gas. This considerably lowers the absorption of radiation and increases the efficiency of grafting.

Another approach involves the addition of a small amount of polyfunctional monomer which mediates the attachment of homopolymer radicals to the grafted substrate.

Since heterogeneous grafting depends on the mutual solubility of the reacting components and on the rate of diffusion of monomer into the polymer, diluents and swelling agents may affect it significantly. On slight swelling of the polymer, the grafting zone gradually moves from the surface into the bulk, and the reaction is accelerated accordingly.

The overall radiation dose, which determines the average number of radicals formed on the macromolecular backbone, changes the average number of grafted branches along the chain while the intensity of radiation, which determines the instantaneous concentration of radicals in the system, controls the length of the branches. The degree of polymerization of the grafted branches is also affected by transfer reactions of monomer, polymer and solvent.

One way of increasing the grafting efficiency is to irradiate the polymer alone. When monomer is added subsequently, the fraction of macroradicals stabilized in the polymer which initiates grafting increases and it may become the dominant process.

However, since some macroradicals decay during irradiation of the polymer, the efficiency of grafting related to the radiation dose is lower.

This technique may also be accompanied either by reduction of the molecular mass of the polymer or, in an inert atmosphere, by crosslinking of grafted macromolecules. In the presence of air, alkyl macroradicals react with oxygen molecules; the peroxyl radicals formed abstract hydrogen from surrounding molecules and hydroperoxyl groups are formed on the polymer chain. As indicated above, these thermally unstable groups may be used for the chemical initiation of grafting.

2.4.3. Nonradical grafting

The choice of the growth polyreaction for grafting onto the original polymer chains depends on the character of the functional groups present. Solutions of aromatic vinyl polymers give complexes with alkali metals which may initiate the anionic polymerization of monomers. At initiation, a chemical bond between the functional group of, say, poly(vinyl naphthenate) and a growing branch is formed. Similarly, the iodophenyl group in polystyrene, after its reaction with butyl lithium, is transformed into a lithium phenyl complex which may initiate the anionic polymerization of acrylonitrile. Grafting by an anionic mechanism is highly efficient and can be used to regulate the number and length of the branches. [21]

2.4.4. Determination of grafting efficiency

The ratio of grafted and overall quantity of polymerized monomer is called the grafting efficiency. It depends on the reactivity of the grafted macromolecule, on the initiator used, on the concentration ratio of polymer to monomer as well as on the temperature, the solubility of the various components of the reacting system and many other factors.[21]

Pure graft copolymer is often isolated by selective precipitation from solution or solvent extraction. As with TLC, fractionation according to molecular weight must be avoided, and each fraction should be analyzed to ascertain that only homopolymers are removed. Furthermore, since stable dispersions which cannot be coagulated completely may form, at least some of the polymer remaining in solution should be isolated by evaporation of the solvent. If the analyses of polymer isolated

by coagulation and by evaporation give the same result, the polymer can be isolated by coagulation. In some cases the separation procedure must be repeated several times or by several different methods. The fractions are characterized by turbidimetry, density gradients, differential thermal analysis, radioactive labeling, infrared and NMR spectroscopy, and gel-permeation chromatography (GPC). Pure graft copolymers have also been isolated by preparative scale column adsorption chromatography. [22]

Heat capacities are usually determined by (power-compensated) differential scanning calorimetry (DSC). Specimen and reference material are heated in such a way that both are always at the same temperature ($\Delta T = 0$). DSC measures the temperature dependence of the electric power P that is necessary to compensate caloric effects and thus the temperature dependence of $d\Delta Q/dt$, the change of added heat ΔQ with time (Fig.2.8). Positive signals indicate exothermic effects (crystallization, exothermic chemical reactions) and negative signals endothermic ones (solid-solid transitions, crystal melting, endothermic chemical reactions). The added heat ΔQ allows to calculate the heat difference between specimen and reference, and, if the heat capacity of the reference is known, also heat, enthalpy, and heat capacity of the specimen.[23] End group analysis of grafted monomer by titration is a kind of measurement method of grafting efficiency.[24-25]

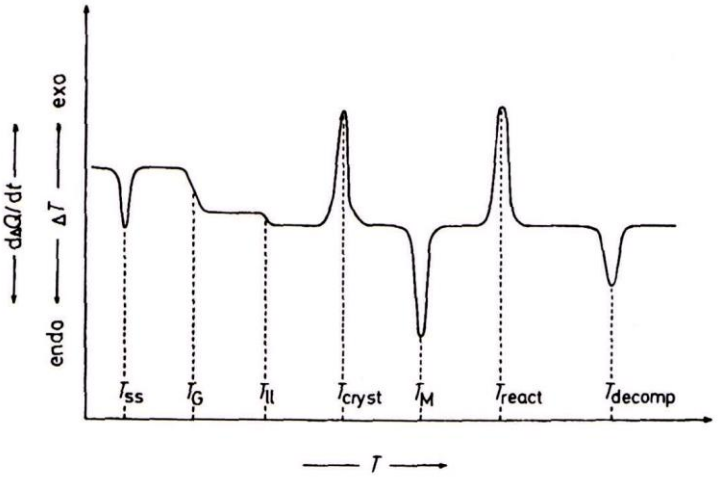


Figure 2.8. Idealized thermogram of a semi-crystalline polymer with solid-solid transition at T_{ss}, glass temperature T_G (transformation of a glass into a melt), liquid-liquid transition at T_{ll} (controversial), crystallization at T_{cryst}, crystalline melting temperature T_M, exothermic reaction at T_{react} and endothermic polymer decomposition at T_{decomp} (schematic).

2.5. Grafting of IA onto Polyolefines

Grafting mechanism runs with the decomposition of peroxide generates radicals, then, they attack the polyolefin to generate polyolefin macroradicals. Polyolefin macroradicals react with IA (Figure 2.9).

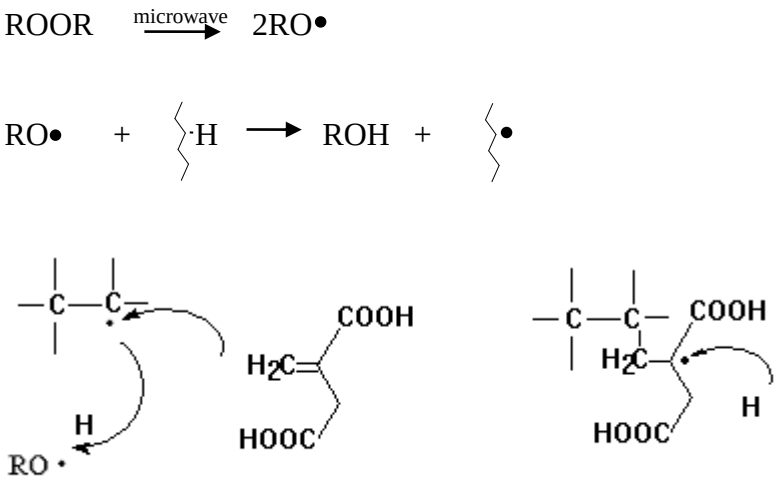


Figure 2.9. Grafting mechanism of IA onto PE

Radical of IA grafted on polymer can use monomer, initiator, macroradical, solvent or polymer to make a proton transfer. Because the reactivity of IA is very low, its homopolymerization is very difficult. Thus, we can say that one macromolecular polyolefinic radical only initiates one IA monomer.

Pesetskii and his coworkers investigated grafting of itaconic acid on low density polyethylene in molten state via reactive extrusion many times in recently years. Pesetskii investigated in these works, initiator and stabilizator efficiency on grafting degree of LDPE with IA. It was shown that initiator solubility affects the grafting degree. The initiators which can be dissolve easily in LDPE, increases the grafting efficiency and the closer the thermodynamic affinity between the peroxide and the monomer, and decreases efficiency of grafting. The stabilizers (e.g.,1,4-dihydroxybenzene) with increased affinity toward the monomer reduce the grafting yield and inhibit crosslinking. At 0.3–0.5 wt % of the stabilizer insoluble in the monomer, the grafting yield can be increased, while inhibiting the LDPE-g-IA crosslinking.[26,27]

In one of these works, it was shown that thermomechanical and rheological properties of LDPE was changed. According to results, while unmodified PE exhibits two glass transition temperatures, modified PE with IA exhibits three glass transition temperatures and with increasing of grafting degree melting temperature increases 1-2 ^{0}C and melt flow rate (MFR) values decrease, it means that viscosity of polymer increases. [28].

In another work of Pesetskii, functionalization of LDPE by grafting of itaconic acid to the macromolecules was found to accelerate its thermal and photo-oxidation in water. The LDPE-g-IA underwent accelerated oxidation in alkaline media whereas no essential changes were detected during testing in acidic media. Under identical thermal conditions films of LDPE would oxidize in water to a greater depth than does in air. Aqueous media containing dissolved stabilizers appear rather efficient. The data suggest that the main cause of the accelerated oxidation of both the virgin and functionalised LDPE in water is a decomposition of macromolecular hydroperoxides initiated by water. These hydroperoxides are formed at the initial stage of the oxygen interaction with the macromolecules. [29]

Pesetskii made his last IA-g-LDPE work in presence of neutralizing agents. When the grafting takes place in the presence of neutralizing agents, the efficiency of the itaconic acid grafting onto macromolecules is found to increase. Neutralization of the grafted itaconic acid contributes to an increase in the mechanical and impact strengths of blends composed of functionalized low-density polyethylene and polyamide-6. [30]

To improve the compatibility and properties of blends based on high-density polyethylene (HDPE) and the ethylene-propylene copolymer (EPR), the functionalization of both through grafting with an itaconic acid derivative, monomethyl itaconate (MMI), was investigated by M.Yazdani and his coworkers. The results show that the grafting reaction increases the toughness and elongation at break of all tested blends and they retained their strength and stiffness. Moreover, the grafted polymers behaved as nucleating agents, accelerating the HDPE crystallization. These results are particularly relevant when both polymeric phases are modified. Morphological studies are in concordance with the mechanical

characterization, showing a reduction of the rubber particle size and a better interfacial adhesion when both polymers are functionalized with MMI. [31]

Yazdani, in another work, synthesized functionalized polypropylene by radical melt grafting either with monomethyl itaconate and dimethyl itaconate to improve its compability of PP with PET. The use of PP grafted with MMI as compatibilizer resulted in even a better dispersion of PP as the minor phase increasing the components interface and there after to an improvement of the adhesion between the two phases. The noncompatibilized blend in this case also showed an even more pronounced two phase behavior as compared with PP/PET blends. The impact resistance of PET in noncompatibilized blend was hardly affected by incorporation of PP. However, when functionalized PP with either MMI or DMI was used as blend compatibilizers, there was an increase of the impact resistance of PET. This probably is due to spesific interactions and/or chemical reaction (transesterification) between the functional groups of the compatibilizer with the blend constituents resulting in a finer dispersion of the minor phase leading to improved interfacial adhesion. [32]

Grafting of maleic anhydride (MAH) onto atactic and isotactic polypropylene by reactive extrusion or in a molten state was investigated a few times. One of these works is grafting of MAH onto PP by styrene-assisted melt free-radical method using a single-screw extruder. The effects of styrene and initiator concentrations on the grafting reaction have been investigated. The results show that the addition of styrene to the melt-grafting system as a comonomer could significantly enhance MAH graft degree onto PP. However, the melt flow rate (MFR) value of the grafted PP is the highest at maximum grafting ratio. This implies that the interaction and reaction between MAH and styrene monomers plays an important role in the grafting reaction. Styrene improves the grafting reactivity of MAH and also reacts with MAH to form the St-MAH copolymer (SMA) before the two monomers graft onto PP. Grafting of SMA onto PP greatly enhanced the graft degree of MAH. [33]

Effect of polyolefin structure on MAH grafting has been investigated in another work, a series of polyolefines with different ethene/propene ratios has been grafted with maleic anhydride (MA) both in the melt and in solution. According to experimental results, the MAH graft content is low for polyolefines with high propene content, increases as the propene content decreases and reaches a plateau at propene levels below 50 wt.%. Branching/crosslinking occurs for polyolefines with

low propene content, while degradation is the main side reaction for polyolefines with a high propene content.[34]

In a study which was made on functionalization of isotactic polypropylene with maleic anhydride by reactive extrusion, it was found that the initial radicals, due to homolitic scission of dicumyl peroxide could be combined with maleic anhydride (MAH) monomers as well as polypropylene (PP) molecular chains. The homopolymerization of MAH cannot occur and the MAH radicals undergo a dismutational reaction under the processing condition (180-190^0 C). [35]

One of the grafting reactions of MAH was worked onto LDPE in a solution medium by microwave assisting system in recently year. The reaction of maleic anhydride (MAH) grafted onto low density polyethylene (LDPE) in xylene solvents in the presence of benzoyl peroxide (BPO) as an initiator by microwave irradiation has been investigated. The influence of reaction conditions such as initiator content, monomer content and irradiation time have been examined. IR spectra of PE and PE-g-MAH show that MAH is really grafted on the PE in a xylene solution by means of microwave. Moreover, the melting temperature of PE-g-MAH is lower than that of PE, but the melting enthalpy of PE-g-MAH higher than that of PE.[36]

In one of the studies which were made with atactic PP, PP was grafted with mixture of α-methylstyrene (MS) and maleic anhydride (MAH). It was shown that MS can not homopolymerize at high temperatures and that MAH and MS tend to copolymerize alternatively. As a result, two grafted PP products are obtained, of which the major is only slightly but the minor is heavily grafted. In another study which was made atactic PP, it was found that under certain reaction conditions MAH takes part in the radical degradation of polypropylene after it is grafted.[37-38]

In a rheological study of PE, effect of maleated polyethylene on the rheological properties of LLDPE/clay nanocomposites has been investigated. It was shown that the nanocomposites of adding a MA-g -PE showed unusual rheological properties such as high shear thinning tendency and elastic property. [39]

2.6. Rheological Behaviour of Polymers

Rheology tries to describe the temporal relationships between forces and deformations of bodies by so-called constitutive equations. Polymers respond in a very complex way to deformation; no comprehensive constitutive equations that have been amended empirically by correction factors.[23,40]

If a force per unit area s causes a layer of liquid at a distance χ from a fixed boundary wall to move with a velocity υ, the viscosity η is defined as the ratio between the shear stress s and the velocity gradient $\partial\upsilon/\partial\chi$ rate of shear γ:

$$\sigma = \eta \frac{\partial \upsilon}{\partial \chi} = \eta\gamma \qquad (2.5)$$

If η is independent of the rate of shear, the liquid is said to be Newtonian or to exhibit ideal behavior. Two types of deviation from Newtonian flow are commonly observed in polymer solutions and melts. One is shear thinning, a reversible decrease in viscosity with increasing shear rate. Shear thinning results from the tendency of the applied force to disturb the long chains from their favored equilibrium conformation, causing elongation in the direction of shear. An opposite effect, shear thickening (dilatancy), in which viscosity increases with increasing shear rate, is rarely observed in polymers. A second deviation from Newtonian flow is the exhibition of a yield value, a critical stress below which no flow occurs.[41] These fluids are named Bingham bodies and behave as either Newtonian fluids or non-Newtonian fluids. Shear-thinning is some times called pseudo-plasticity because of similarity to a Bingham body although there is no yield value. Flow curves which shown below explain flow behaviors. (Figure 2.10.) [23]

Several flow equations are summarized in Table 2.2 for various models. Here σ_0 is the yield stress, η_0 the viscosity at lower shear rates and η_∞ at the higher shear rates, and α and n are constants.[42]

Table 2.2. Flow models and equations

Model	Equation
Newtonian	$\sigma = \eta\gamma$
Bingham plastic	$\sigma - \sigma_0 = \eta\gamma$
Power law	$\sigma = \eta\gamma^n$
Power law with yield value	$\sigma - \sigma_0 = \eta\gamma^n$
Casson fluid	$\sigma^{1/2} - \sigma_0^{1/2} = \eta_\infty^{1/2}\gamma^{1/2}$
Williamson	$\eta - \eta_\infty = \frac{(\eta_0 - \eta_\infty)}{1 + \sigma/\sigma_m}$
Cross	$\eta - \eta_\infty = \frac{(\eta_0 - \eta_\infty)}{1 + \alpha\gamma^n}$

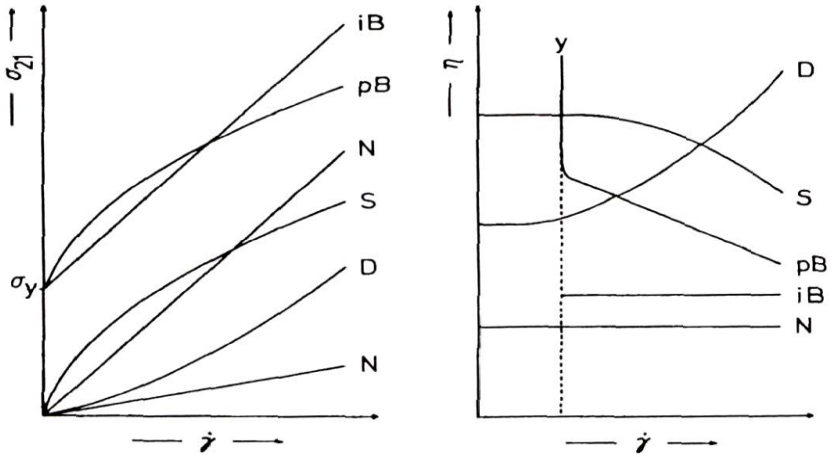


Fig 2.10. Dependence of shear stress σ_{21} and dynamic shear viscosity η on the shear rate γ for Newtonian (N), shear-thickening (D), and shear-thinning (S) liquids and for ideal (iB) and pseudoplastic (pB) Bingham bodies. σ_y =Yield value.

Methods commonly used for measuring the viscosity of polymer solutions and melts are listed in Table 2.3

Table 2.3. Summary of methods for measuring viscosity

Method	Approximate Useful Viscosity Range, Poises
Capillary pipette	10^{-2}–10^{3}
Falling sphere	1–10^{5}
Capillary extrusion	1–10^{8}
Parallel plate	10^{4}–10^{9}
Falling coaxial cylinder	10^{5}–10^{11}
Stress relaxation	10^{3}–10^{10}
Rotating cylinder	1–10^{12}
Tensile creep	10^{5}–$>10^{12}$

An elementary capillary rheometer (extrusion plastometer) is used to determine the flow rate of polyethylene in terms of melt index, defined as the mass rate of flow of polymer through a specified capillary under controlled conditions of temperature and pressure.

Rotational viscometers are available with several different geometries, including concentric cylinders, two cones of different angles, a cone and a plate, or combination of these. [41]

Cone and plate rheometer is the important method of measuring the rheological properties of polymer solutions and melts. The cone angle, θ, is typically very small and at these low angles, the shear rate is given as

$$\gamma = \frac{W}{\theta} \qquad 2.6$$

Where W is the angular velocity of the cone. The shear stress, τ, is determined as

$$\tau = \frac{3T}{2\pi R^3} \qquad 2.7$$

Where Table 2.3. summary of methods for measuring viscosity is the measured torque on the cone having radius R.[43]

The parallel-disk system (Figure 2.11.) is very similar in operation to the cone-and-plate device. When the upper disk is rotated with constant angular velocity W, the torque T required to achieve this rotation as well as the total force required to maintain the disks at a separation H, and the pressure distribution $(p + \tau_{zz})|_{z=0}$ across one of the plates can be measured.

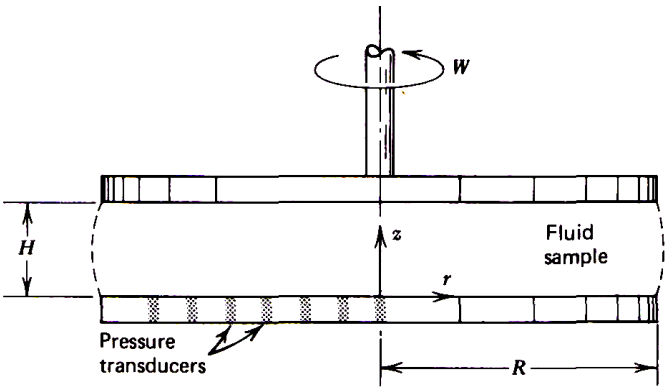


Figure 2.11. Parallel-disk instrument (Parallel-disk rheometer)

A mathematical modeling of the plate-and-plate rheometer can be derived in a few steps.

First step is finding velocity distribution using laminar Newtonian flow between parallel plane surface problem (Figure 2.12);

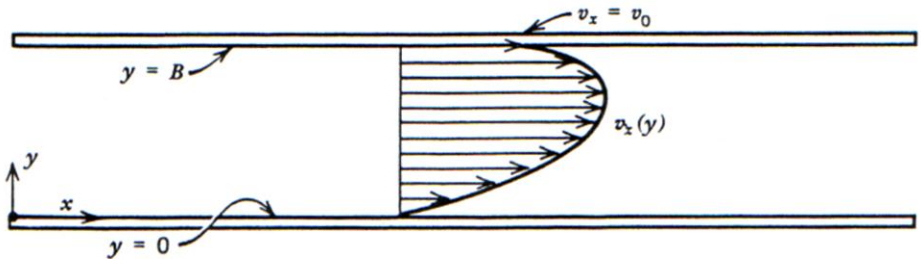


Figure 2.12. Flow between horizontal parallel planes with the upper plane moving and with an imposed pressure gradient in the flow direction.

In this system $V_x=V_x(y)$, $V_z=0$, $p=p(x,y)$. An additional contribution to the fluid motion is that due to a constant applied pressure gradient $\partial p/\partial x$.

The x-component of the equation of motion;

$$\tau = \tau_0 + \mu \frac{dV_x}{dy} \quad \Rightarrow \quad \frac{d\tau}{dy} = \mu \frac{d^2 V_x}{dy^2} \qquad \textbf{2.8}$$

$$-\frac{\partial p}{\partial x} + \mu \frac{d^2 V_x}{dy^2} = 0 \quad \Rightarrow \quad \frac{1}{\mu}\frac{\partial p}{\partial x} = \frac{d^2 V_x}{dy^2} \qquad \textbf{2.9}$$

$$\int \frac{d^2 V_x}{dy^2} dy = \frac{1}{\mu} \int \frac{\partial p}{\partial x} dy \quad \Rightarrow \quad \frac{dV_x}{dy} + A = \frac{1}{\mu}\left(\frac{\partial p}{\partial x} y + C\right) \qquad \textbf{2.10}$$

$$V_x + A.y = \frac{1}{\mu}\left(\frac{\partial p}{\partial x}\frac{y^2}{2} + C.y + D\right) \qquad \textbf{2.11}$$

Boundary condition at $y= 0$ $V_x=0$ for $D=0$

$$V_x = \frac{1}{\mu}\left(\frac{\partial p}{\partial x}\frac{y^2}{2} + (C-A\mu)y\right) \qquad \textbf{2.12}$$

Boundary condition at $y= B$ $V_x=V_0$

$$V_0\mu = \frac{\partial p}{\partial x}\frac{B^2}{2} + (C-A\mu)B \Rightarrow (C-A\mu)B = V_0\mu - \frac{\partial p}{\partial x}\frac{B^2}{2} \Rightarrow C = \frac{1}{B}\left(V_0\mu - \frac{\partial p}{\partial x}\frac{B^2}{2}\right) + A\mu$$

2.13

$$V_x = \frac{1}{\mu}\left\{\frac{\partial p}{\partial x}\frac{y^2}{2} + \frac{1}{B}\left(V_0\mu - \frac{\partial p}{\partial x}\frac{B^2}{2}\right)y\right\} \qquad \textbf{2.14}$$

$$V_x = \frac{1}{\mu}\left\{\frac{\partial p}{\partial x}\left[\frac{y^2}{2} - \frac{By}{2}\right] + V_0\left[\frac{y}{B}\right]\right\} \qquad \textbf{2.15}$$

$$V_x = \frac{B^2}{2\mu}\frac{\partial p}{\partial x}\left[\left(\frac{y}{B}\right)^2 - \left(\frac{y}{B}\right)\right] + V_0\left(\frac{y}{B}\right) \Longrightarrow V_x = V_0\left(\frac{y}{B}\right) - \frac{B^2}{2\mu}\frac{\partial p}{\partial x}\left[\frac{y}{B} - \frac{y^2}{B}\right]$$

2.16

The result is the velocity distribution:

$$V_x = V_0\left(\frac{y}{B}\right) - \frac{B^2}{2\mu}\frac{\partial p}{\partial x}\left\{\left(\frac{y}{B}\right) - \left(\frac{y}{B}\right)^2\right\} \qquad \textbf{2.17}$$

Second step is identification the shearing surfaces as fluid planes of constant z; each shearing surface is rotating with an angular velocity w(z) that depends on its position between the two disks. The velocity field is then $V_\theta = rw(z)$, $V_r = 0$, and $V_z = 0$; accordingly, the shear rate is $\gamma = r\, dw/dz$.

If fluid inertia is neglected, the equation of motion in cylindirical coordinates takes the form:

r-component $$0 = -\frac{\partial p}{\partial r} - \left[\frac{1}{r}\frac{\partial}{\partial r}(r\tau_{rr}) - \frac{\tau_{\theta\theta}}{r}\right] \qquad \textbf{2.18}$$

θ-component $$0 = -\frac{\partial}{\partial z}\tau_{\theta z} \qquad \textbf{2.19}$$

ϕ-component $$0 = -\frac{\partial p}{\partial z} - \frac{\partial \tau_{zz}}{\partial z} + \rho g_z \qquad \textbf{2.20}$$

Where we have set $\tau_{r\theta}=\tau_{rz}=0$ in accordance with symmetry requirements .Equation 2.19 says that the shear stress, and hence the shear rate, is independent of z.

Thus the expression for the shear rate given above can be integrated to yield w, which in turn gives;

$$V_\theta = \frac{rw_z}{H} \qquad \textbf{2.21}$$

Thus the shear rate is a function of r alone:

$$\gamma = \frac{rw_z}{H} \qquad \textbf{2.22}$$

In order to find the viscosity of the sample, we consider the total torque T required to rotate the upper disk:

$$T = 2\pi \int_0^R (-r\tau_{z\theta})\, r\, dr \qquad \textbf{2.23}$$

$$= 2\pi \int_0^R \eta\gamma\, r^2\, dr \qquad \textbf{2.24}$$

$$= 2\pi \frac{R^3}{\gamma_R{}^3} \int_0^{\gamma_R} \eta(\gamma)\gamma^3\, r^2\, d\gamma \qquad \textbf{2.25}$$

$\gamma_R = \gamma(R)$ is the shear rate at the rim of the device. By differentiating this last result with respect to γ_R it is found:

$$\eta(\gamma_R) = \frac{(T / 2\pi R^3)}{\gamma_R} \left(3 + \frac{d \ln(T / 2\pi R^3)}{d \ln \gamma_R} \right) \qquad \textbf{2.26}$$

Thus by varying γ_R and computing the change in torque as indicated above, the viscosity function may be determined explicitly.[44-45]

2.6.1. Rheological properties of LDPE and LLDPE

The rheological properties of LLDPE, because of its linear structure and narrow molecular weight distribution, are different from those of conventional LDPE. LLDPE film extrusion resins have a narrow molecular weight distribution. Their molecular configuration is essentially linear with short-chain branching and little or no long-chain branching. These resins exhibit shear flow behavior typical of linear polymers having a narrow molecular weight distribution. Figure 2.13 shows the shear viscosity-shear rate behavior of similar-melt-index LDPE and LLDPE film extrusion resins.

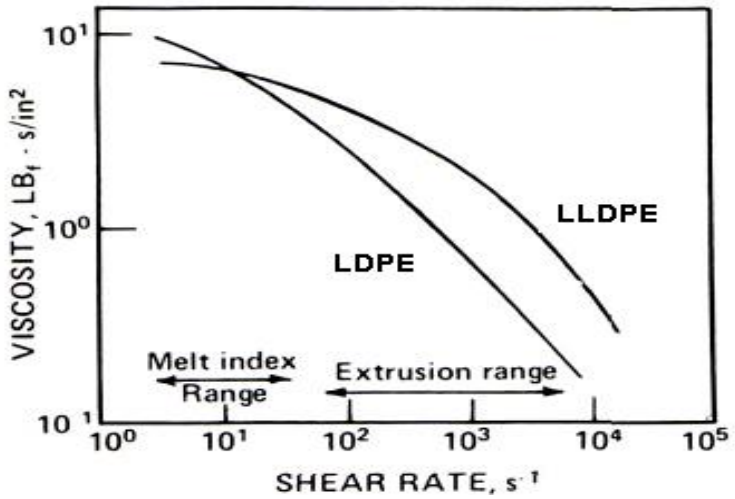


Figure 2.13. The viscosity under shear of LDPE and LLDPE of the same melt index.

The LLDPE melt shows a quite different extensional behavior. Extensional viscosity is significantly lower than for LDPE, and it shows no unbounded stress growth. The LLDPE melt exhibits little strain-hardening when strain rates are low. [46]

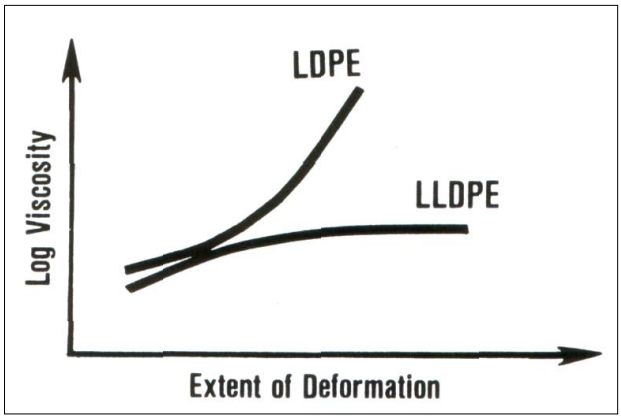


Figure 2.14. Extensional behavior of polyethylene melts

Relative to HP-LDPE, narrow-molecular-weight-distribution, LLDPE melts can be described as "stiff in shear and "soft" in extension. Figure 2.14 compares the behavior of LDPE and LLDPE during melt extension as they exit the die.

Tensile strength of LLDPE is 50 to 75% higher and elongation at least 50% higher than those of LDPE. Other properties such as impact strength and puncture resistance are also greater for LLDPE. Figure 2.15 compares the ultimate tensile strength of conventional LDPE resins and LLDPE resins.

LLDPE has a higher modulus at equal density; Figure 2.16 represents a comparison of modulus versus density for the two types of LDPE.

LLDPE has a broader temperature use range than LDPE. Figure 2.17 shows a comparison of melting points of the two types of resin. LLDPE melts at a 10-15^{0}C higher temperature. It also has better low temperature impact strength than LDPE.

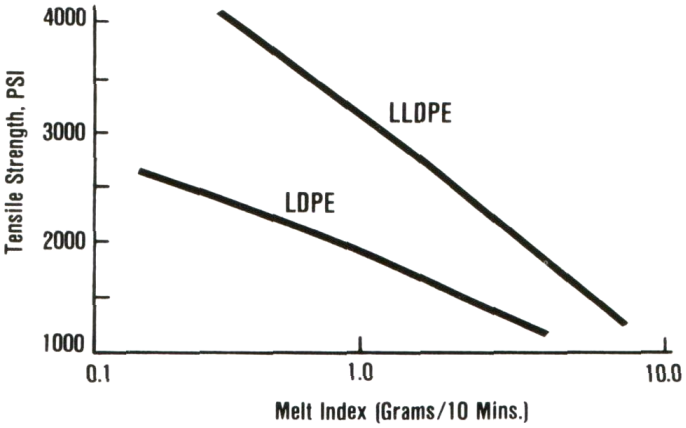


Figure 2.15. The ultimate tensile strength of conventional LDPE resins and LLDPE resins.

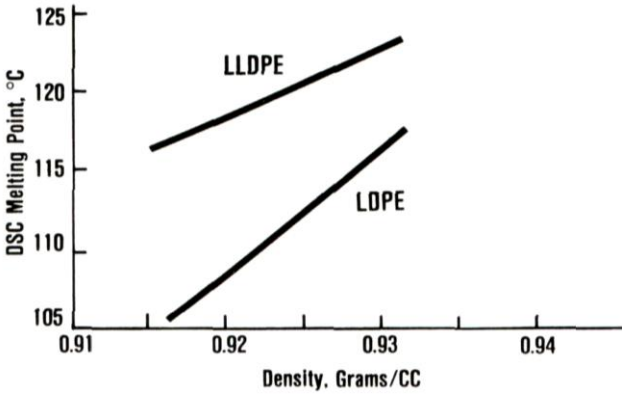


Figure 2.16. Modulus versus density for LDPE and LLDPE

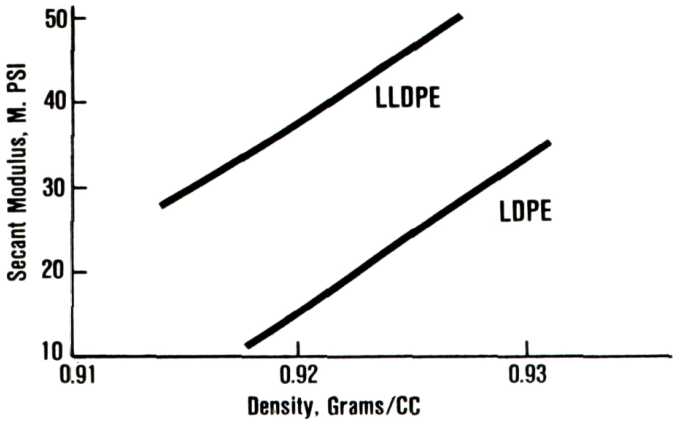


Figure 2.17. Melting point versus density for LDPE and LLDPE

3. EXPERIMENTAL PART

3.1. Chemicals Used

3.1.1. Polyolefines

3.1.1.1. Low density polyethylene (LDPE)

Low density polyethylene (G03-5) was obtained from PETKIM Petrochemical Holding. Its number averaged and weight averaged molecular weights were 20,300 g/mol and 213,600 g/mol, respectively.

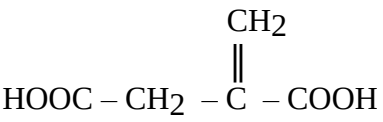
3.1.1.2. Linear low density polyethylene (LLDPE)

Linear low density polyethylene was obtained from Exon Corp. Its density was 0.91-0.925 g/ cm^3.

3.1.1.3. Isotactic polypropylene (i-PP)

Isotactic polypropylene (MH418) was obtained from PETKIM Petrochemical Holding. Its number averaged and weight averaged molecular weights were 53,300 g/mol and 565,700 g/mol, respectively.

3.1.2. Itaconic acid



Systematic name, 2-methylene succinic acid which was the product of Fluka A. G. With a 99% purification, was used without any purification procedure. (m.p. = 165-167 ^{0}C)

3.1.3. Itaconic monoesters

Monomethyl itaconate, monobutyl itaconate and monooctyl itaconate was used as monoesters which has been prepared before by the procedure which is described below.

Preparation Mono Methyl Itaconate

To a mixture of 25 g IA and 25 cc methanol, 0.5 cc acetyl chloride was added with shaking. The mixture was refluxed on the steam-bath for 20 minutes, solution taking place at the boiling point. The excess methanol was immediately evaporated in vacuum. The residue was recrystallized from 50 cc of benzene by addition of 75 cc of heptane and chilly to 0^0C.

Preparation Mono Butyl Itaconate

To a mixture of 25 g IA and 50 cc butyl alcohol, 0.5 cc acetyl chloride was added with shaking. The mixture was refluxed on the steam-bath for 20 minutes, solution taking place at the boiling point. The excess methanol was immediately evaporated in vacuum. The residue was recrystallized from 70 cc of benzene by addition of 30 cc of heptane and chilly to 0^0C.

Preparation Mono Octyl Itaconate

To a mixture of 25 g IA and 100 cc octyl alcohol, 1 cc acetyl chloride was added with shaking. The mixture was refluxed on the steam-bath for 2 hours, solution taking place at the boiling point. The excess alcohol was immediately evaporated in vacuum. The residue was recrystallized from petroleum ether.

3.1.4. Dibenzoyl peroxide (DBPO)

It was used as the initiator, which is a product of Peroxide Chemie GmbH (München, Germany).

3.1.5. Xylene

It was used as the solvent, which is a product of Merck A.G.,

3.1.6. Isopropyl alcohol

It was used for analytical measurements as the solvent, which is a product of Merck A.G.

3.1.7 Methyl alcohol

It was used for precipitation of reacted samples, obtained from Merck A.G.

3.1.8. Ethyl alcohol

It was used for analytical measurements as the solvent, which is a product of Merck A.G.

3.1.9. Potasiumhydroxide (KOH)

It was used for analytical measurements purchased from Merck A.G.

3.1.10. Hydrochloric acid (HCl)

% 37 HCl solution, which is a product of Merck A.G., was used for analytical measurements.

3.1.10. Sodiumcarbonate ($Na_2CO_3. H_2O$)

It was used for analytical measurements purchased from Merck A.G.

3.1.11. Bromothymol blue

It was used as the indicator for back titration of product samples.

3.1.12 Methylene red

It was used as the indicator for standardizing titration solutions.

3.2. Equipment Used

3.2.1. Magnetic stirrer with heater

It was used for heating and mixing of product sample in xylene solvent for analytical measurement work. This instrument has a maximum mixing rate of 1250 rpm and it can be heated to a maximum temperature of 300°C.

3.2.2. Microwave oven

Vestel MD 930 model MW applicator has the sizes as 335x339x245 mm (WxHxD), energy outgoing power as 1000 W and MW frequency as 2.45 GHz. This oven has ten MW levels at the range of 10-100. All experiments were run at first level, which is equal to 100 W power, fixing the temperature to 140^0C.

3.2.3. Vacuum drying oven

WTC Binder model oven used at the 60^0C to remove the residual methanol and xylene on grafted polymer samples.

3.2.4. Fourier transform infrared spectrophotometer (FTIR)

Infrared spectra of samples were recorded a Jasco FTIR-5300 Fourier Transform infrared spectrometer.

3.2.5. Differential scanning calorimeter (DSC)

In this study, DSC-5 model machine, which is thermal analysis data station of Shimadzu TA-501, was used.

3.2.6. Parallel plate rheometer

TA Instruments AR2000 model rheometer has the geometry as 25 mm ETC aluminum parallel plate, 1000 μm gap. Data and measurements were obtained by means of software program named “Rheology Advantage”.

3.3. Experimental procedure

3.3.1. Preparation and purification of grafted polyolefines

All grafting reactions were carried out at 140 ^{0}C with 100 W microwave input power. Polyolefin was dissolved in xylene then was mixed together with DBPO and monomer in a certain proportion. In all experiments, the weight ratio of xylene to polyolefines is always 10/1.

A little amount of ethanol was added to mixture in order to dissolve monomers better in the reaction solution. The mixtures are put into the microwave applicator, irradiated for the expected time, and then removed. The samples were purified by dissolving in xylene and precipitating in methyl alcohol two times to be sure of the removal of unreacted monomers, and then dried in vacuum at 60^{0}C. The products were used to determine the grafting ratio (GR) and to test IR, DSC and rheological properties.

3.4. Tests and Analyses

3.4.1. Measurement of grafting ratio by analytical method

A small amount (0.2-0.4g) of grafted polyolefin was dissolved and heated to 110°C with reflux in 100 mL xylene for 30 min, followed by cooling to 60°C. 30 milliliters 0.005 N potassium hydroxide (KOH)/ethanol solution was added, and the mixture was heated under reflux for 15 min. The alkali concentration was determined by acid titration using 0.005 N hydro-chloride (HCl)/ isopropanol solution. The indicator was 0.1% bromothymol blue/ethanol solution. A blank was carried out by the same method.

Grafting degree is expressed by the following equation:

$$GR = \frac{N x (V_0 - V) x M_W}{n x W x 1000} x 100\ \% \qquad (3.1)$$

where N is the concentration of HCl/ isopropanol(mol/L), W is quantity of sample (g), V is the volume of HCl/ isopropanol used by titration, V_0 is the volume of HCl/ isopropanol used in a blank assay, M_W is the molecular weight of monomer and n is the number of carboxyl group on the monomer.

3.4.2. Fourier transform infrared spectroscopy (FTIR) analyses

Grafted LDPE, LLDPE and i-PP samples were characterized by FTIR. The samples were prepared by hot presses method at thickness of 100μm.

3.4.3. Differential scanning calorimetric (DSC) analyses

The Tm values were determined from the curves in the related temperature zones in the termograms in order to make a precise estimation to observe very small changes in the melting temperature values. The rate flow was 50 ml/min, heating rate was 10^0C in all experiments.

3.4.3. Rheological analyses

The rheological studies of samples were carried out by the plate-and-plate rheometer at 190 ^{0}C. All experiments were run at the range of 0.01-100 Hz frequency, 0.002-0.500 1/s shear rate, 200-15,000 (Pa) shear stress.

4. RESULTS AND DISCUSSION

4.1. Synthesis Conditions

In this work, that has been studied to graft LDPE, LLDPE and isotactic PP, which are commercial polymers with antioxidant, with IA and its monoesters. 29 samples were synthesized by the method that is referred in experimental procedure section 3.3.1.

4.1.1. Optimisation of reaction conditions

Pre-works were done in order to determine optimum conditions for synthesis of samples that were used to examine their thermal and rheological properties.

In the optimization experiments, LDPE and IA were used as the polymer and the monomer respectively and the DBPO was chosen as the suitable initiator because of its low activation temperature as compared with dicumyl peroxide, which is commonly used in grafting of polyolefines. In addition, for determination of influence of DBPO content on the grafting degree, the experiments were done with DBPO weight ratio to LDPE within the range of 0.35 - 1.20 % at 1% weight ratio of IA (Table 4.1, Fig 4.1). Moreover, the influence of IA content on grafting degree was investigated working with weight ratio of IA to LDPE within the range of 1-5 % at 0.75 % weight ratio of DBPO (Table 4.2, Fig 4.2). In these experiments, reaction period was held in a constant value as 10 minutes. Further more, the influence of reaction period on grafting degree was determined with prolonging irradiation time within the time range of 4-14 min., as which IA content was taken 1% weight ratio of IA to LDPE and DBPO content was taken 0.75 % weight ratio of DBPO to LDPE (Table 4.3, Fig 4.3) . Consequently, optimization conditions were determined as 0.75 % weight ratio of initiator (DBPO) to polymer (LDPE) and 2% weight ratio of monomer (IA) to polymer (LDPE) with 10 minutes reaction period.

4.1.2. Synthesis conditions of characterization samples

LDPE, LLDPE, i-PP were grafted with itaconic acid (IA) and its monoesters (MMI,MBI, and MOI) by using the optimization conditions improved for the grafting reaction of LDPE with IA. The experiments that were carried out at equal amount moles of monoesters had given results at the different grafting ratios (Table 4.4, 4.5, 4.6). Thus, the monomer contents of itaconic acid and monoesters in reaction medium were arranged in such a way that the mole carboxyl groups/weight percent of grafting ratios are nearly the same for a better comparison of their thermal and rheological properties. Grafting ratios of LDPE, LLDPE and i-PP which were used in rheological and thermal characterization are shown in Table 4.7, 4.8, 4.9. In addition, LDPE was grafted with MBI using three different monomer (IA) contents and predetermined optimization conditions to obtain LDPE-g-MBI samples. These three different grafting ratio values were proposed as approximately 0.0020%, 0.0030%, 0.0040% mol /100 g LDPE. The experimental grafting ratios of LDPE-g-MBIs are shown in Table 4.10. The monomer contents of itaconic acid in reaction medium were arranged in such ways that the mole carboxyl groups/weight percent of grafting ratios are sequential (from the lowest to the highest). Rheological properties of these samples were compared with each other by rheological analyses.

4.2. Evaluation of Experimental Results

The influence of DBPO content on the grafting degree can be seen on Fig 4.1. At the very low DBPO concentrations, grafting does not occur because of the antioxidant in LDPE. The plot shows that the grafting ratio (GR) increases significantly with the increasing of DBPO to 0.75 w/w %. However, after 0.75 w/w %, GR goes to be leveled.

The results of experiments about monomer concentration show that the grafting ratio increases with the increase of IA content, but the percent conversion decreases (Fig 4.2). When the radical concentration is constant, the collision chance of IA and macromolecule increases with the increase of IA content, leading to the increase of grafting degree. However, when IA concentration is increased, GR is not increased with the same ratio, leading to the decrease of percent conversion.

The relationship between irradiation time (polymerization period) and the grafting degree is shown in Fig 4.3. It can be seen that the grafting degree increases significantly with prolonging the irradiation time within the time range of 6 -10, whereas it falls after 10 minutes. We can say that the longer irradiation time causes to increase the temperature, but we know that IA has a ceiling temperature. (Polymerization tendency decreases at high temperature.)

Monomer, initiator, macroradical, solvent or polymer can transfer a proton to radical of IA grafted on PE. Because the grafted polymer is soluble, it can be seen that the any crosslinking does not occur during the reaction period. Amount of initiator is few; a transfer is possible only with solvent. Because the reactivity of IA is very low, its homopolymerization is very difficult. Thus, we can say that one macromolecular polyolefinic radical only initiates one IA monomer.

The Table 4.4, 4.5, 4.6, show the grafting conversions and grafting ratios of grafted LDPE, LLDPE and i-PP with IA and monoesters. According to these results, we can say that monoesters are more capable of grafting onto polyolefines as compared with IA. In addition, with increasing of side chain length on estergroup, the grafting ability of ester decreases.

When the grafting ratios of grafted LDPE, LLDPE and i-PP are compared with each other, it is shown that grafting values of LLDPE are lower than those of LDPE and the grafting ratios of i-PP are close to those of LDPE.

4.3. FTIR Analyses

LDPE and grafted LDPE samples were characterized by FTIR.

The FTIR spectra of all samples can be seen in Figure 4.4-4.6. When the spectrum of LDPE without grafting (Fig 4.4) and other spectra of all grafted samples (Fig 4.5,4.6) are compared with each other, it can be seen that the sizes of the carbonyl peaks are very short because the grafting degree of samples are very low. Thus, quantitative analysis of grafted samples by means of FTIR will not be clear.

In conclusion, IR spectra results show that the grafting samples exhibit a characteristic vibration band of the carbonyl group (1730 cm^{-1}). The bands verify that IA and its monoesters are really grafted onto polyolefines.

4.4. DSC Analyses

The melting temperature values of the grafted samples are determined by differential scanning calorimetry analyses. The thermograms of the samples given in Table 4.7 of LDPE can be seen in Figure 4.7.

The thermogram of LDPE shows that melting temperature of LDPE at 113.5^0C decreases gradually by increasing the side chain length of the ester groups of comonomers.

The thermograms of the samples given in Table 4.9 of i-PP can be seen in Figure 4.8. The thermogram of i-PP shows that melting temperature of i-PP at 163.5^0C decreases gradually by increasing the side chain length of the ester groups of comonomers. However, on DSC results of i-PP, there is not a big difference between the melting temperature of MMI-g-PP and IA-g-PP (Fig.4.8).

4.5. Rheological Analyses

The rheological properties of samples were carried out by the plate-and-plate rheometer. The rheological results of the grafted and ungrafted LDPE, LLDPE, and i-PP samples are given in Fig. 4.9-4.36. Viscosity and modulus curves are derived from the data, which is obtained working at the constant frequency and shear rate values. When viscosity, shear stress and shear rate curves are investigated (Fig 4.9, 4.10, 4.23, 4.24, 4.30, 4.31), Newtonian and Power Law regions can be seen. Newtonian region is seen at very low shear rate values and the viscosity in this region is constant. Zero shear viscosity can be measured from Newtonian region. In the Power Law region, viscosities decrease with increasing of shear rate. Power Law index (n) values that were calculated from Power Law region and zero shear viscosity values that were calculated from Newtonian region were given in Table

4.11., 4.12., 4.13. It can be said that samples exhibit shear thinning (pseudo plastic) behavior, since the Power Law index (n) is less than 1.

In the viscosity-shear rate curve of LDPE (Fig 4.10), at the low shear rate values unmodified polymer has the lowest viscosity value. The grafting of IA, MMI, MBI and MOI increases the viscosity of polymer.

Melt viscosities of LDPE-g-MBI, LDPE-g-IA, LDPE-g-MMI, and LDPE-g-MOI at 190^0C, decrease, respectively.

At the low frequencies, storage modulus (G') values of LDPE-IA and LDPE-g-MBI are higher than those of LDPE. It means that their elasticities are higher than that of LDPE. At the high frequencies, elasticity of LDPE is higher than those of LDPE-IA and LDPE-g-MBI, LDPE-g-MMI, and LDPE-g-MOI. (Fig 4.12)

Loss modulus (G'') values of LDPE-IA and LDPE-g-MBI are higher than those of LDPE at frequencies until 0.05 Hz. (Fig.4.13) Los modulus values of LDPE-g-MBI, LDPE-g-IA, LDPE-g-MMI, and LDPE-g-MOI are lower than those of LDPE at frequencies higher than 0.05 Hz. In conclusion, we can say that at frequencies higher than 0.5 Hz, storage modulus (G') and loss modulus (G'') of LDPE are higher than those of LDPE-g-MBI, LDPE-g-IA, LDPE-g-MMI, and LDPE-g-MOI.

A log-log plot of G' vs G'' is very nearly linear (Fig 4.14) and Fig 4.15 gives complex viscosity –frequency curve of modified and unmodified LDPE.

On the viscosity-shear rate curve of LDPE's samples in different grafting ratio values, 0.0022%, 0.0033% and 0.0040% mol/100 g LDPE , which have been grafted with MBI, the three grafted samples show approximately the same tendency until the shear rate value of 0.027 1/s and the viscosity values are higher than those of the unmodified LDPE (Fig.4.17) It is seen clearly on the shear rate-shear stress graph, the curves of unmodified LDPE and LDPE with 0.0040% grafting ratio coincide with each other and all the curves combine on the highest shear rate value after the shear rate value of 0.054 1/s.(Fig.4.18)

In the storage modulus (G')-frequency curve (Fig.4.19), it is observed that, until the frequency value of 8 Hz the curves of LDPE samples with 0.0033% and 0.0040% grafting ratio coincide with each other and the G' values of unmodified LDPE is

lower than those of the sample with 0.0022% grafting ratio and higher than those of the others until frequency value of 2.5 Hz. On the Loss modulus (G'')-Frequency graph (Fig.4.20), the G'' values of unmodified LDPE is higher than those of the others after frequency value of 2.5 Hz. On the log log plot of G''- G', the plot is very close to linear (Fig.4.21). Fig 4.22 gives complex viscosity – frequency curve of grafted with MBI and unmodified LDPE.

At the shear rate and shear stress curves of LLDPE and modified LLDPEs (Fig 4.23 and 4.24), we can see that unmodified LLDPE has the lowest viscosity values. LLDPE-g-MBI and LLDPE-g-MMI nearly have the same rheological properties. While LLDPE-g-IA has the higher viscosity values than those of the LLDPE-g-MBI and LLDPE-g-MMI until shear rate value of 0,4 1/s , it cross with them and begins to decrease after this value. At the shear rate curve for beginning LLDPE-g-MOI has same viscosity values with LLDPE-g-IA but after a short time, viscosity values of LLDPE-g-IA begin to decrease. LLDPE-g-MOI has higher viscosity values than those of the others and at the end of curve combines with the others.

At the low frequencies, storage modulus (G') values of LLDPE-IA, LLDPE-g-MMI, LLDPE-g-MBI and LLDPE-g-MOI are higher than those of LDPE. It means that their elasticities are higher than that of LLDPE. After 15,78 Hz, all of them connect and have the same storage modulus values and elasticity properties are equal (Fig 4.26.). Loss modulus (G'') curves of all LLDPEs coincide at the all frequency values (Fig 4.27).

At log-log plot of G' vs G'',for beginning LLDPE and LLDPE-g-IA show different tendency at the opposite ways. After the 3 logaritmic value of G' the plot turns to linear (Fig 4.28.) and Fig 4.29 gives complex viscosity –frequency curve of modified and unmodified LLDPE.

In the shear rate and shear stress curves of unmodified i- PP and modified i-PPs, it can be seen that unmodified i-PP has the highest viscosity value and i-PP-g-MOI has the lowest viscosity value. After viscosity values of i-PP, viscosity values of i-PP-g-IA, i-PP-g-MMI and i-PP-g-MBI decrease respectively (Fig 4.30- 4.32).

At the all frequencies, storage modulus (G') and loss modulus (G'') values of i-PP is higher than those of others. It means that its elasticity is higher than those of the

others. i-PP-g-MOI does not give G cross-over point (Fig 4.33, 4.34). In Table 4.14 G cross-over point values of all i-PP samples can be observed.

At log-log plot of G' versus G'' for low frequency values, i-PP-g-MOI shows different tendency as compared with the others. After the 3 Pa (log value of G') i-PP-g-MOI coincides with the others (Fig.4.35) and same tendency can be shown on complex viscosity –frequency curve of modified and unmodified i-PP (Fig 4.36)

When all curves of different polymers are compared with each other, it can be seen that while viscosity values of i-PP decrease obviously by grafting, viscosity values of LDPE and LLDPE increase by grafting but this increasing is not significant. This condition can be observed easily in Fig 4.37 and Fig 4.38.

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APPENDIX. TABLES OF EXPERIMENTAL RESULTS

Table 4.1. Reaction conditions for determination of initiator concentration effect to grafting ratio of LDPE-g-IA

Sample No.	DBPO, % (g/100 g LDPE)	Grafting Ratio, % (g /100 g LDPE)
1	0.35	0.0095
2	0.40	0.0380
3	0.50	0.0880
4	0.60	0.1088
5	0.75	0.1233
6	1.00	0.1300
7	1.20	0.1330

([IA]= 1 g /100 g LDPE, T=140^{0}C, MW power = 100 W, t=10 min.)

Table 4.2. Reaction conditions for determination of monomer concentration effect to grafting ratio of LDPE-g-IA

Sample No.	IA, % (g /100 g LDPE)	Grafting Ratio, % (g /100 g LDPE)	Conversion, % (g/100 g LDPE)
5	1	0.1230	12.30
8	2	0.1450	7.250
9	3	0.1699	5.660
10	4	0.1830	4.575
11	5	0.1928	3.856

([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power = 100 W, t=10 min.)

Table 4.3. Reaction conditions for determination of reaction period effect to grafting ratio of LDPE-g-IA

Sample No.	Time (min.)	Grafting Ratio, % (g / 100 g LDPE)
12	4	0.03244
13	6	0.07065
14	8	0.10970
5	10	0.12330
15	12	0.09547
16	14	0.03604

([IA]= 1 g /100 g LDPE , [DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power = 100W)

Table 4.4. Grafting ratio and % conversions of LDPE with IA and monoesters in optimum conditions

Sample No.	Monomer	Monomer Concentration in React. Medium (mol /100 g LDPE)	Grafting Ratio, % (mol /100 g LDPE)	Grafting Ratio, % (g / 100 g LDPE)	Conversion, % (g/100 g LDPE)
8	IA	0.01538 mol (2.0 g)	0.001115	0.145	7.25
17	MMI	0.01538 mol (2.2 g)	0.002232	0.321	14.52
18	MBI	0.01538 mol (2.9 g)	0.001997	0.371	12.98
19	MOI	0.01538 mol (3.7 g)	0.001674	0.405	10.88

([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power = 100 W)

Table 4.5. Grafting ratio and % conversions of LLDPE with IA and monoesters in optimum conditions

Sample No.	Monomer	Monomer Concentration in React. Medium (mol /100 g LLDPE)	Grafting Ratio, % (mol /100 g LLDPE)	Grafting Ratio, % (g / 100 g LLDPE)	Conversion, % (g/100 g LLDPE)
20	IA	0.01538 mol (2.0 g)	0.00058	0.0845	4.225
21	MMI	0.01538 mol (2.2 g)	0.001241	0.1728	7.854
22	MBI	0.01538 mol (2.9 g)	0.001185	0.2204	7.600
23	MOI	0.01538 mol (3.7 g)	0.000621	0.1503	4.03

([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power = 100 W)

Table 4.6. Grafting ratio of i-PP with IA and monoesters in optimum conditions and % conversions

Sample No.	Monomer	Monomer Concentration in React. Medium (mol /100 g i-PP)	Grafting Ratio, % (mol /100 g i-PP)	Grafting Ratio, % (g / 100 g i-PP)	Conversion, % (g/100 g i-PP)
24	IA	0.01538 mol (2.0 g)	0.001128	0.1466	7.332
25	MMI	0.01538 mol (2.2 g)	0.002107	0.3034	13.79
26	MBI	0.01538 mol (2.9 g)	0.0018853	0.3506	12.09
27	MOI	0.01538 mol (3.7 g)	0.0014417	0.3489	9.43

([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power = 100 W)

Table 4.7 Grafting ratios of LDPE, which was used in rheological and thermal characterization

Sample No.	Monomer	Grafting Ratio, % (mol /100 g LDPE)
8	IA	0.001115
17	MMI	0.002232
28	MBI	0.002200
29	MOI	0.002200

([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power = 100 W)

Table 4.8 Grafting ratios of LLDPE, which was used in rheological and thermal characterization

Sample No.	Monomer	Grafting Ratio,% (mol /100 g LLDPE)
30	IA	0.000647
31	MMI	0.001200
32	MBI	0.001200
33	MOI	0.001200

([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power = 100 W)

Table 4.9 Grafting ratios of i-PP, which was used in rheological and thermal characterization

Sample No.	Monomer	Grafting Ratio, % (mol /100 g i-PP)
34	IA	0.001200
35	MMI	0.002330
36	MBI	0.002450
37	MOI	0.002107

([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power = 100 W)

Table 4.10 Grafting ratios of LDPE-g-MBI, which was used in rheological characterization

Sample No.	Monomer	Grafting Ratio, % (mol /100 g LDPE)
28	MBI	0.002200
38	MBI	0.003327
39	MBI	0.004054

([DBPO]= 0.75 g /100 g LDPE, T=140^{0}C, MW power = 100 W)

Table 4.11 Power law index (n) and zero shear viscosity values of grafted and ungrafted LDPE samples

Samples	Power law index (n) values	Zero shear viscosity values (Pa.s.)
LDPE	0.5568	59,280
LDPE-g-IA	0.4446	100,800
LDPE-g-MMI	0.5554	73,650
LDPE-g-MBI	0.4220	112,600
LDPE-g-MOI	0.5463	62,040

Table 4.12 Power law index (n) and zero shear viscosity values of grafted and ungrafted LLDPE samples

Samples	Power law index (n) values	Zero shear viscosity values (Pa.s.)
LLDPE	0.6247	805
LLDPE-g-IA	0.6122	1,008
LLDPE-g-MMI	0.6178	962
LLDPE-g-MBI	0.6159	957
LLDPE-g-MOI	0.6115	1,043

Table 4.13 Power law index (n) and zero shear viscosity values of grafted and ungrafted i-PP samples

Samples	Power law index (n) values	Zero shear viscosity values (Pa.s.)
PP	0.3468	15,720
PP-g-IA	0.4421	1,621
PP-g-MMI	0.4692	1,190
PP-g-MBI	0.5380	595
PP-g-MOI	0.7672	86

Table 4.14 Cross-over point values of grafted and ungrafted i-PP samples

Sample	G cross-over point (Pa)	Frequency (Hz)
PP	20,800	2.42
PP-g-IA	27,490	20.38
PP-g-MMI	28,640	28.87
PP-g-MBI	31,790	62.72
PP-g-MOI	no cross-over point	no cross-over point

APPENDIX. FIGURES OF EXPERIMENTAL RESULTS

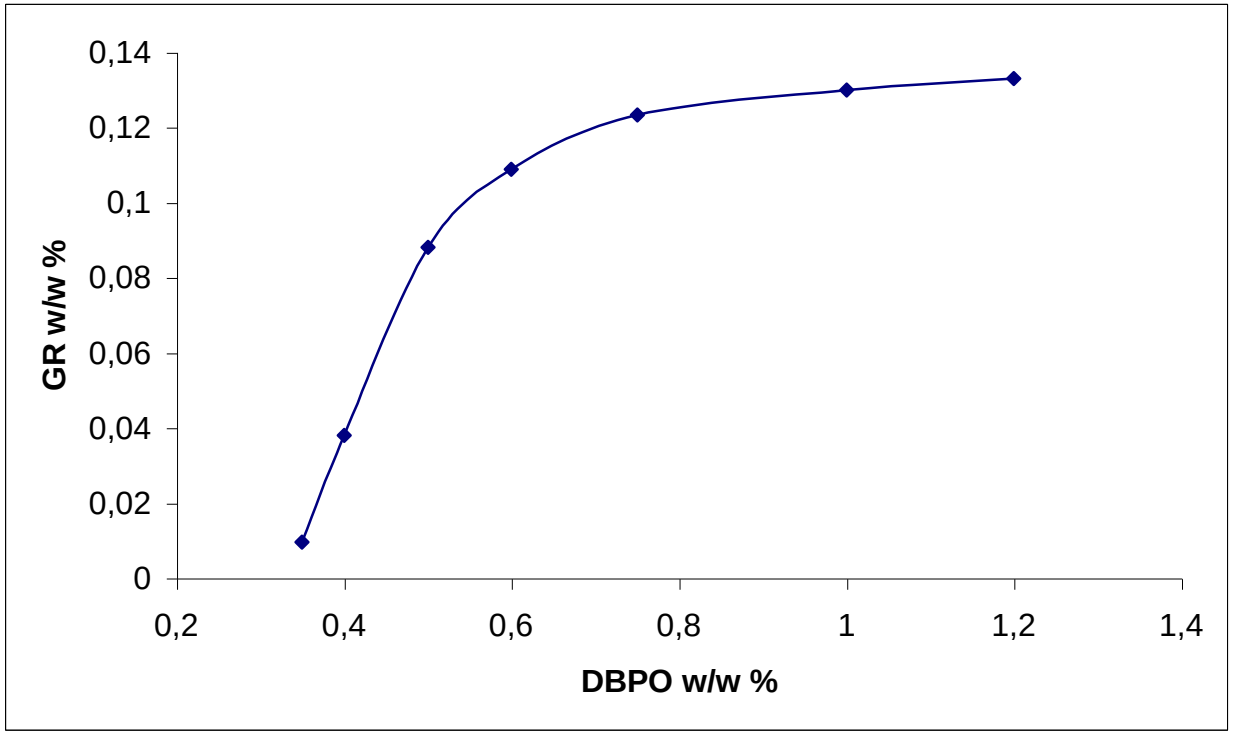

Fig 4.1 Plot of DBPO concentration ([DBPO] w/w %) vs Grafting ratio (GR w/w %)

[IA] = 1 w/w % , t = 10 min, MW power = 100 W

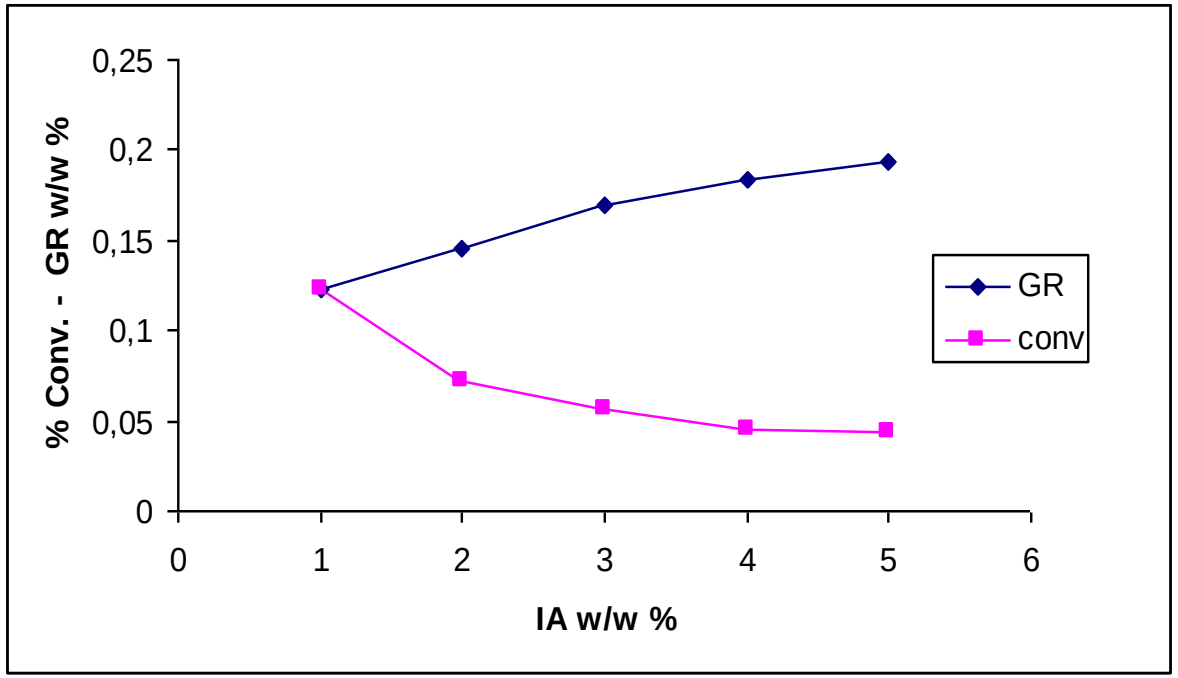

Fig 4.2 Plot of Monomer content ([IA] w/w %) vs Grafting ratio (GR w/w %) and % Conversion)

[DBPO] = 0.75 w/w % t =10 min MW power = 100 W

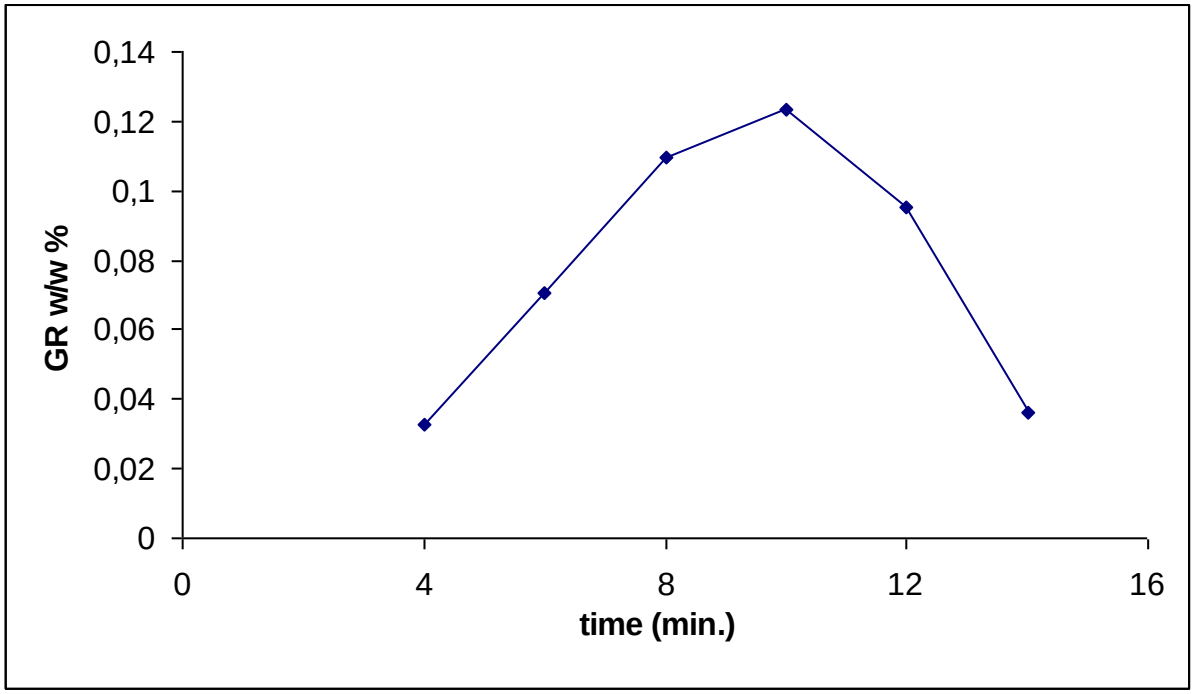

Fig 4.3 Plot of Polymerization period (min.) vs Grafting ratio (GR w/w %)

[DBPO] = 0.75 w/w %, [IA] = 1 w/w % , MW power = 100 W

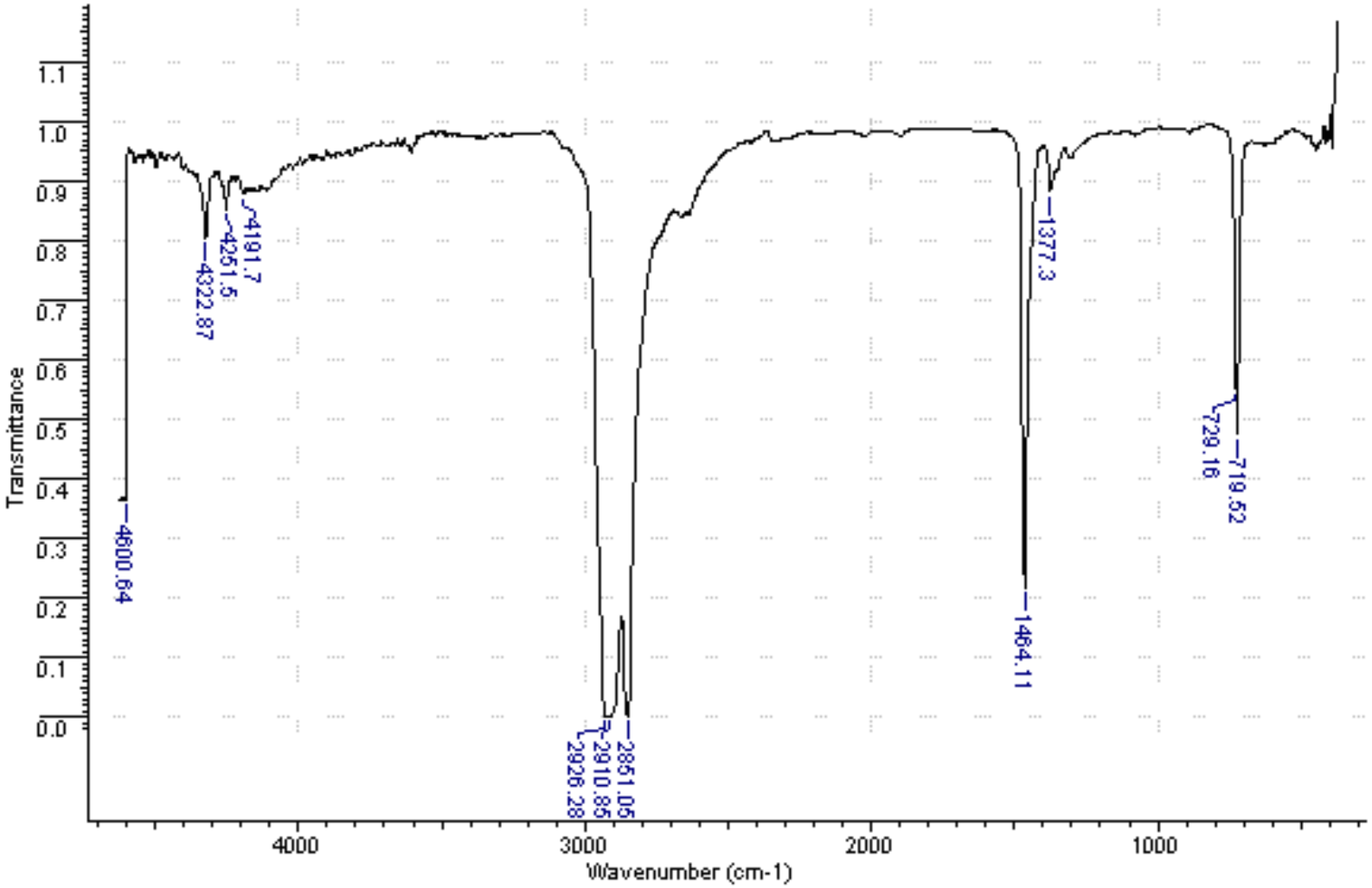

Fig 4.4. FTIR Spectrum of ungrafted LDPE

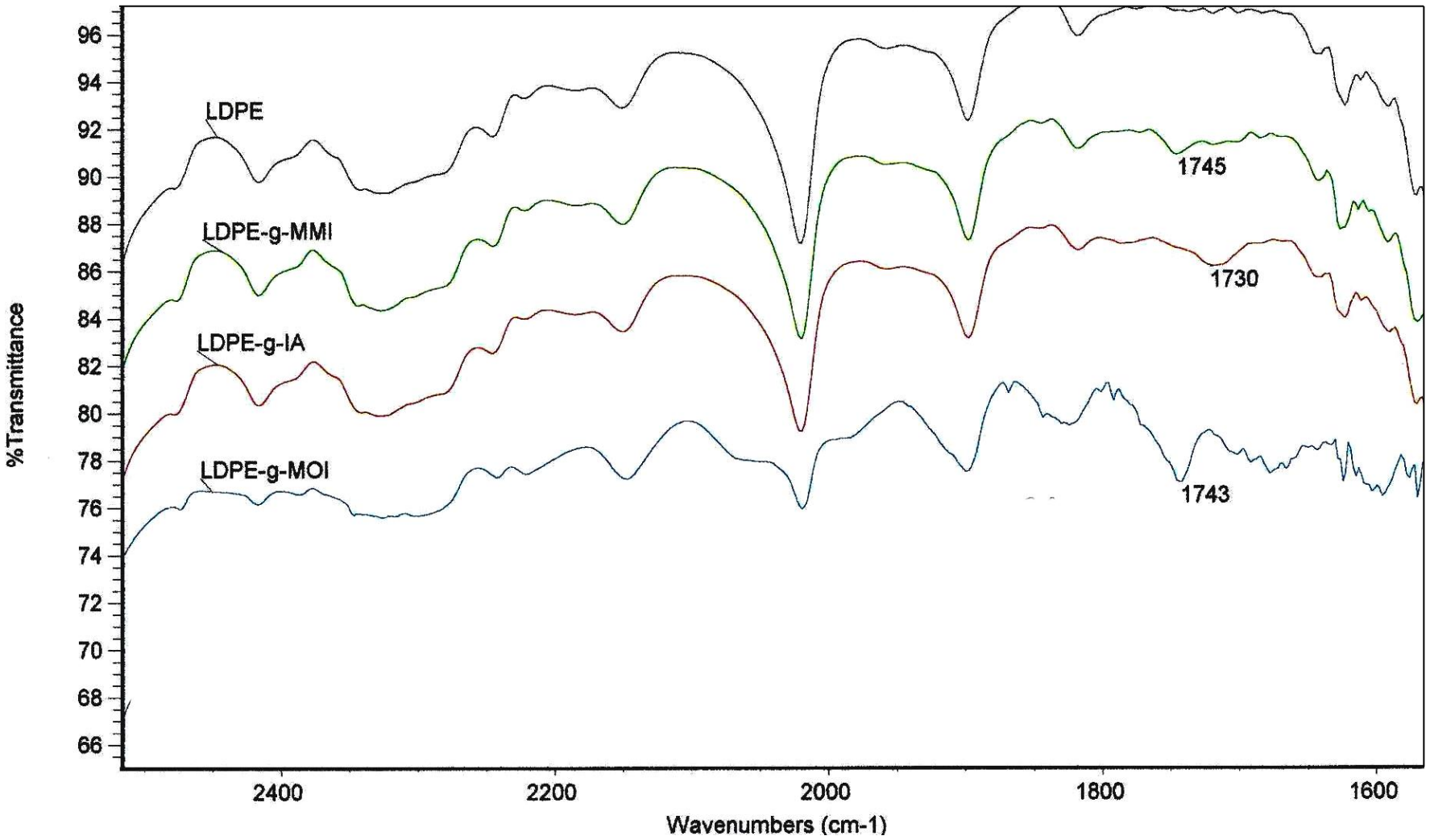

Fig 4.5 FTIR Spectra of ungrafted LDPE and grafted LDPE with IA, MMI, MOI

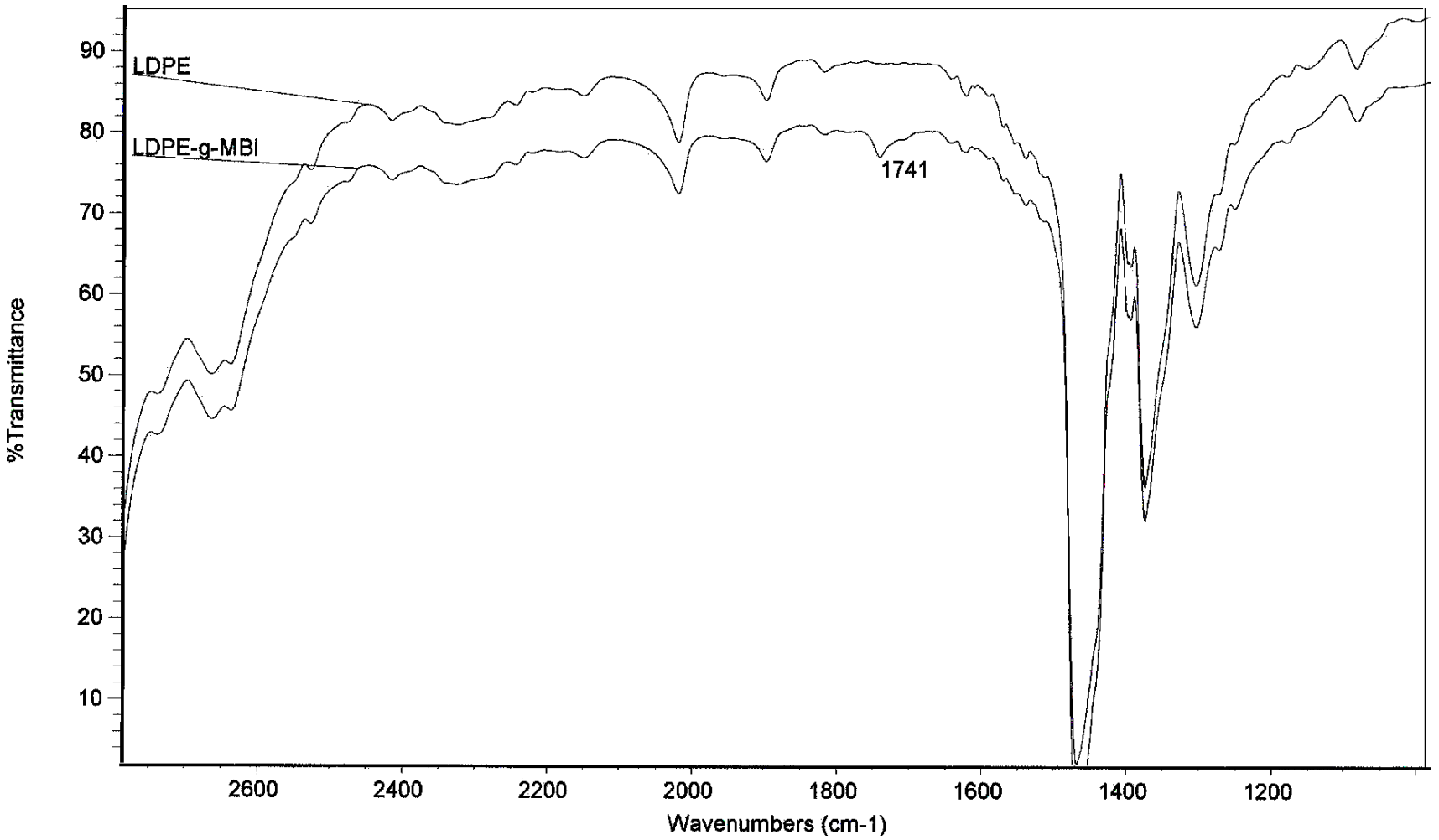

Fig 4.6 FTIR Spectra of ungrafted LDPE and grafted LDPE with MBI

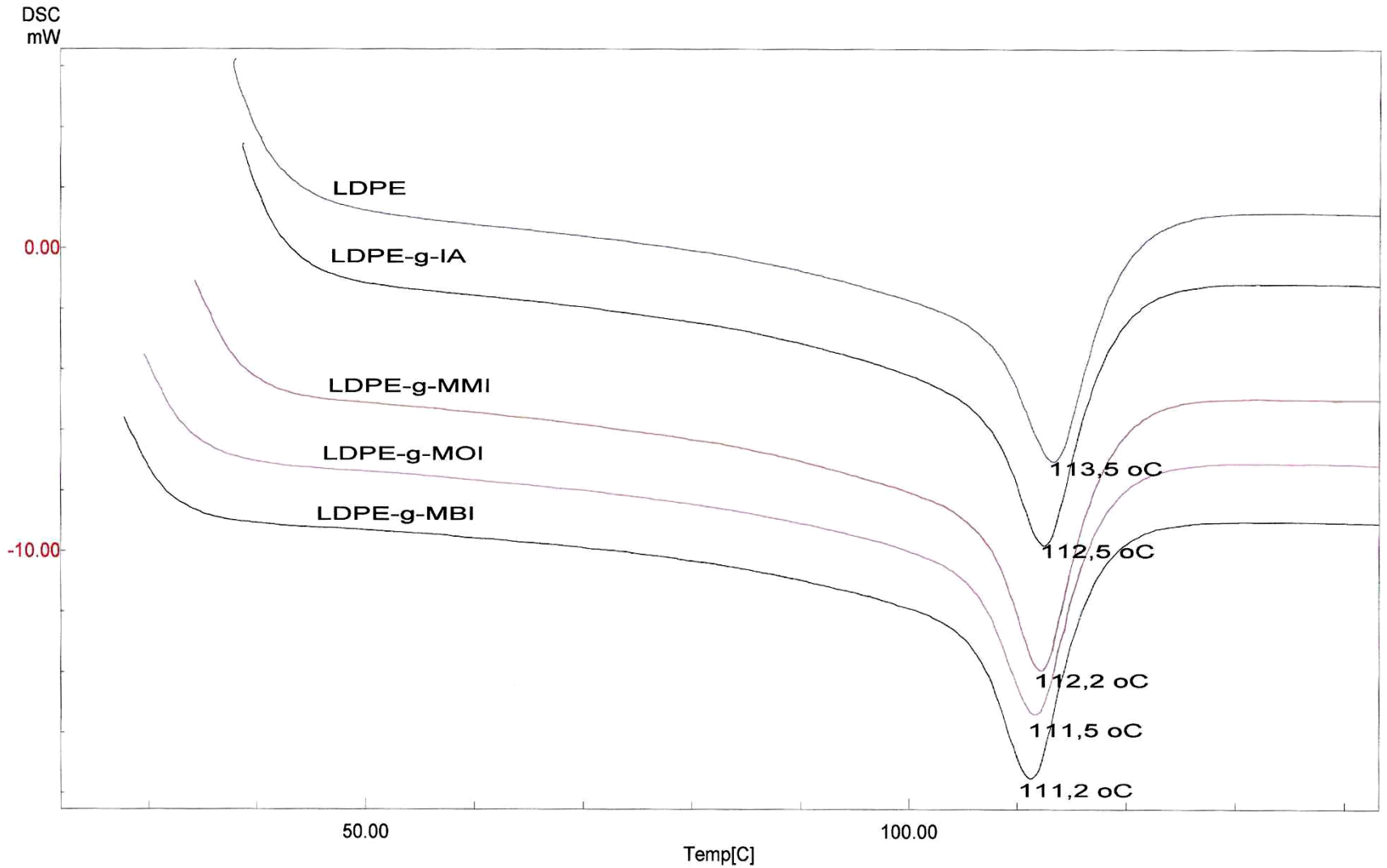

Fig 4.7 DSC Thermograms of ungrafted LDPE and grafted LDPE with IA, MMI, MBI, MOI

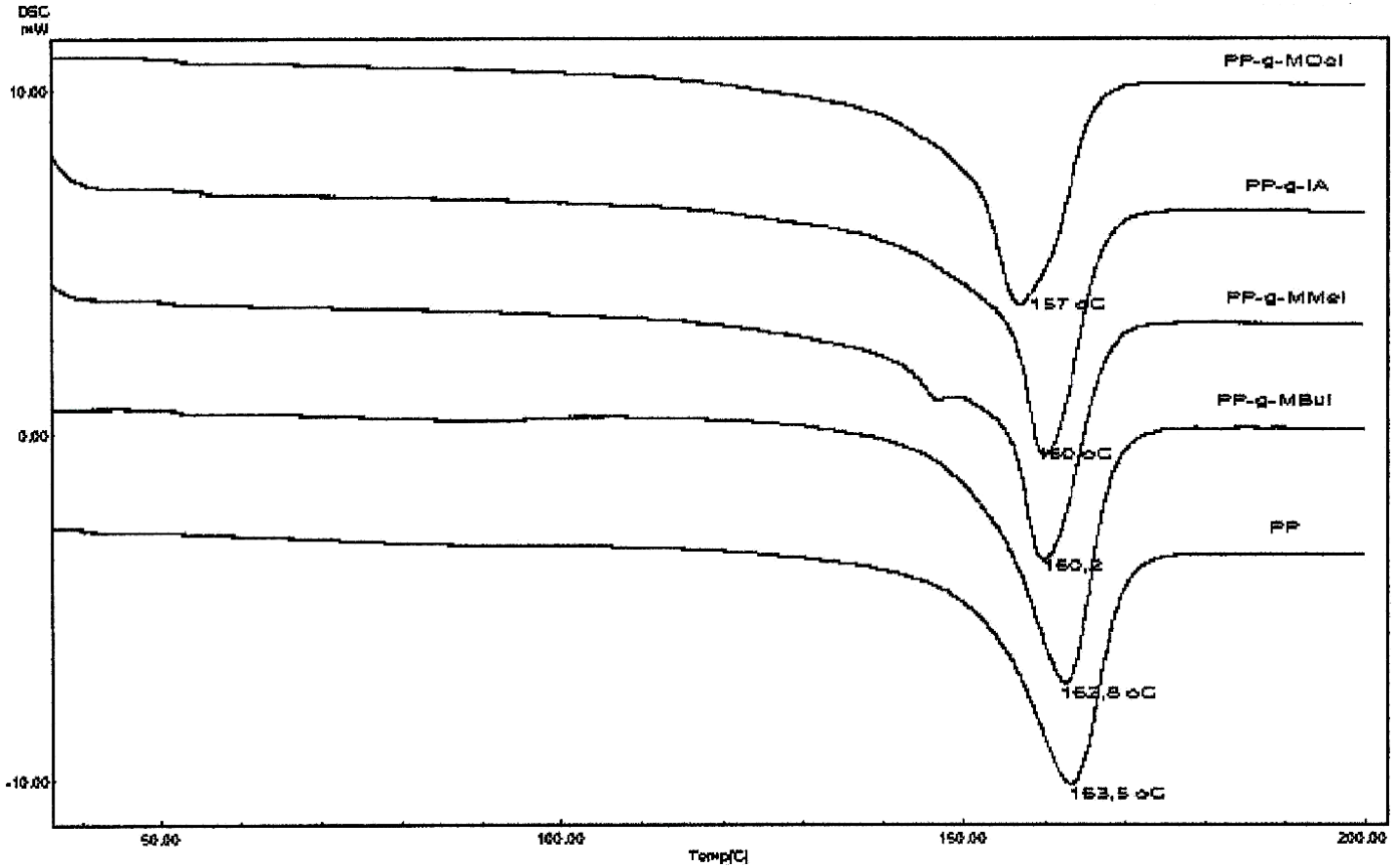

Fig 4.8 DSC Thermograms of ungrafted PP and grafted PP with IA, MMI, MBI, MOI

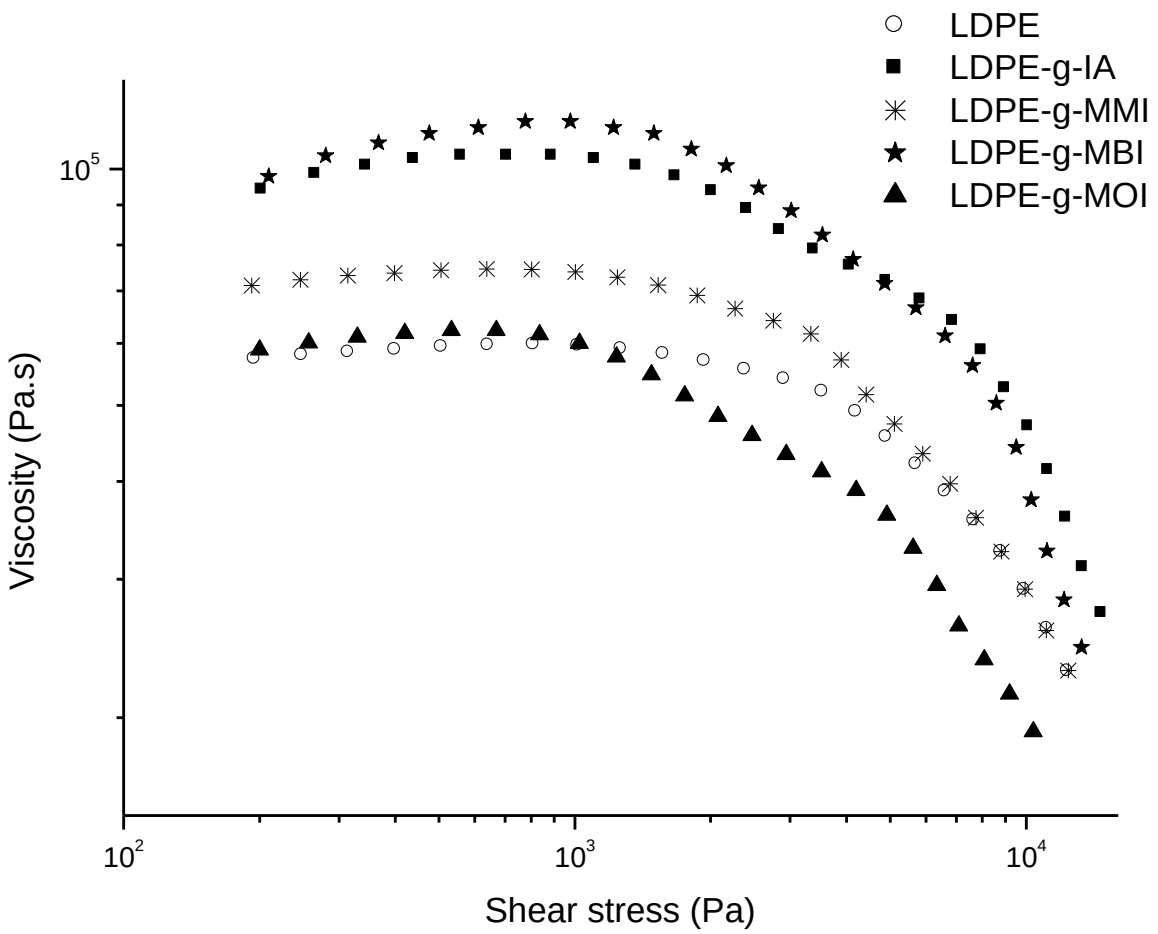

Fig 4.9 Viscosity-Shear stress curve of LDPE and grafted LDPEs

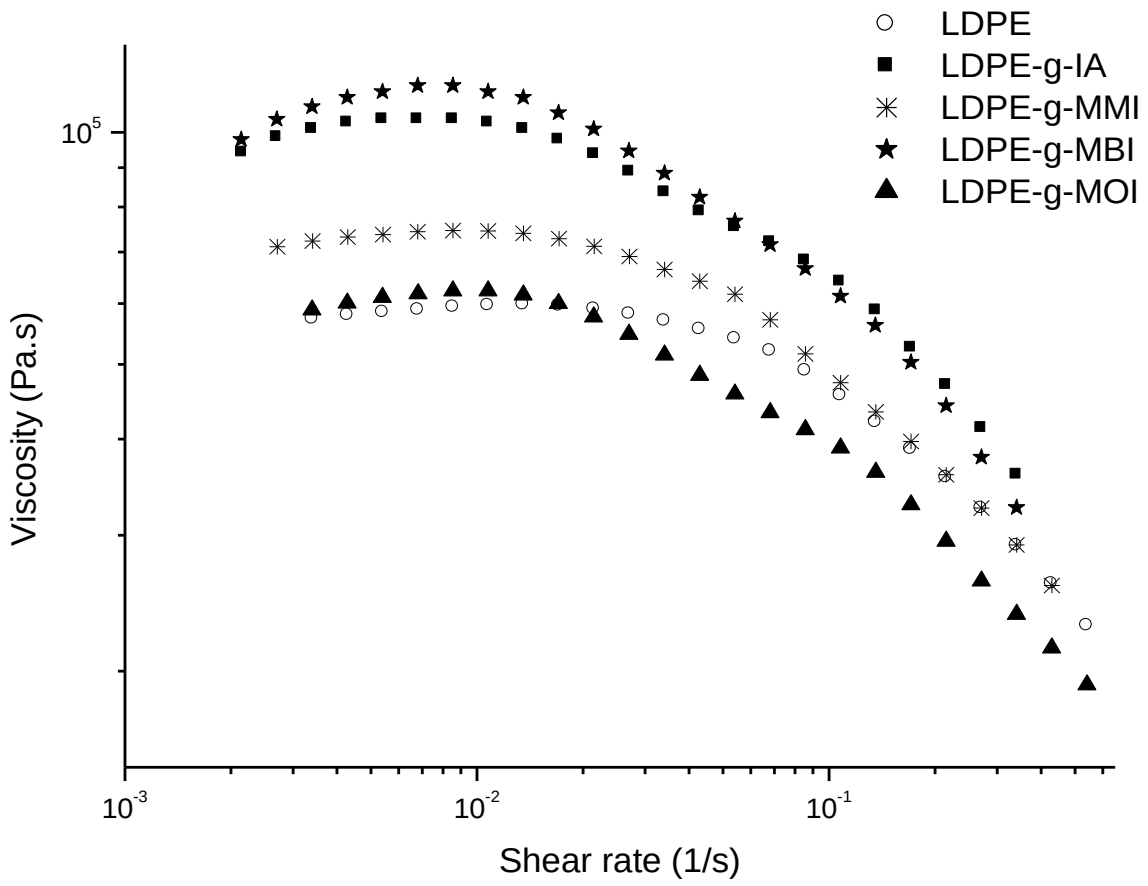

Fig 4.10 Viscosity-Shear rate curve of LDPE and grafted LDPEs

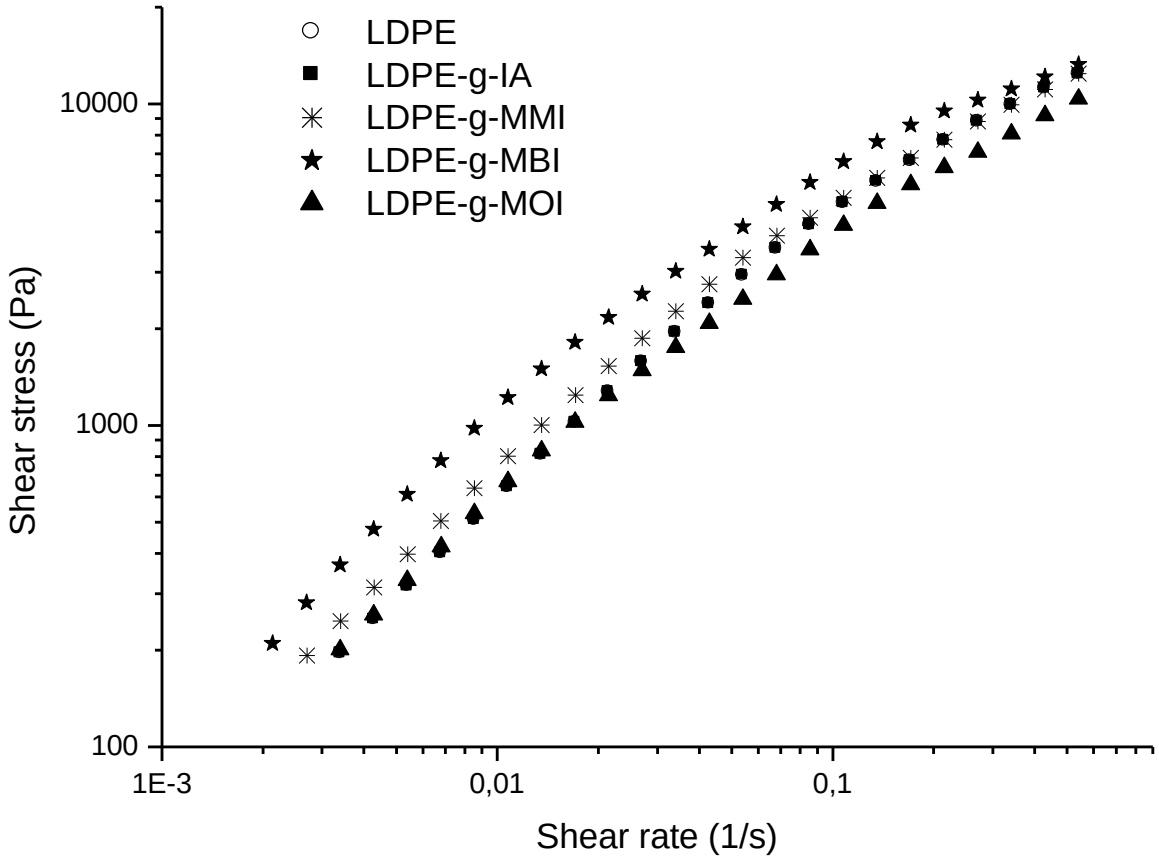

Fig 4.11 Shear Stress-Shear rate curve of LDPE and grafted LDPEs

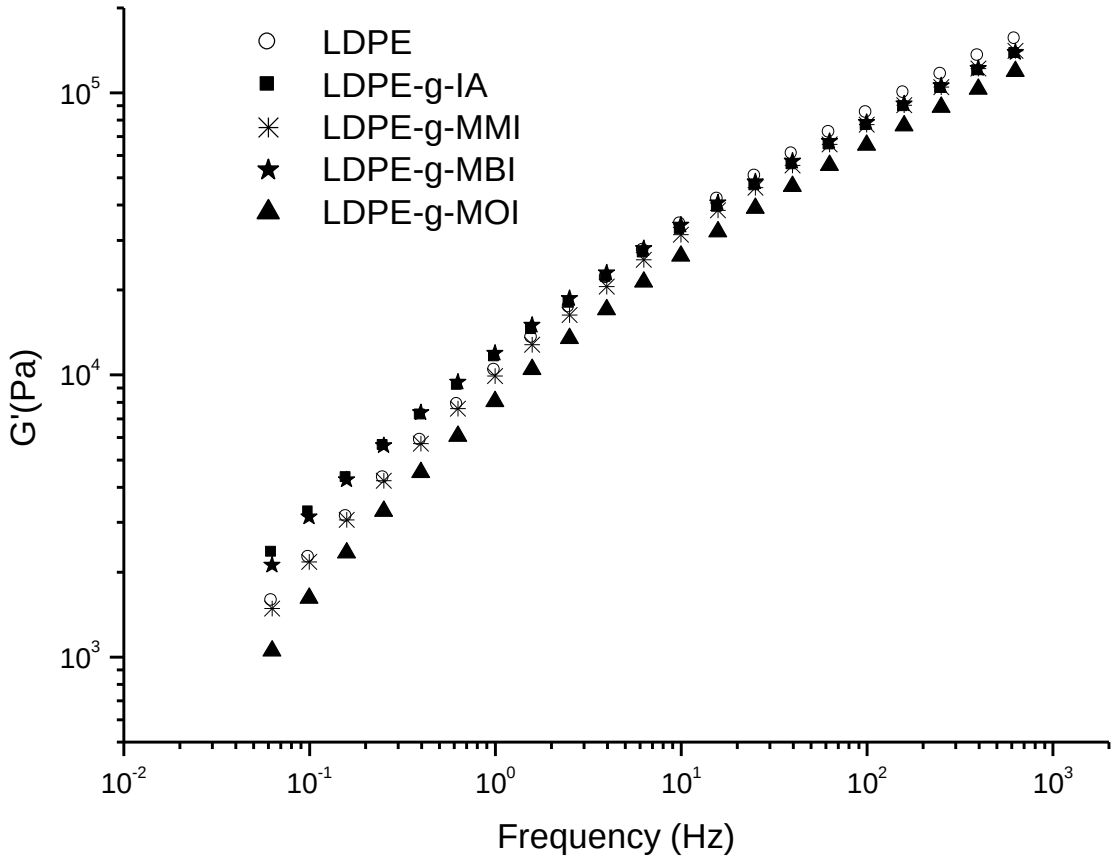

Fig 4.12 Storage Modulus (G')- Frequency curve of LDPE and grafted LDPEs

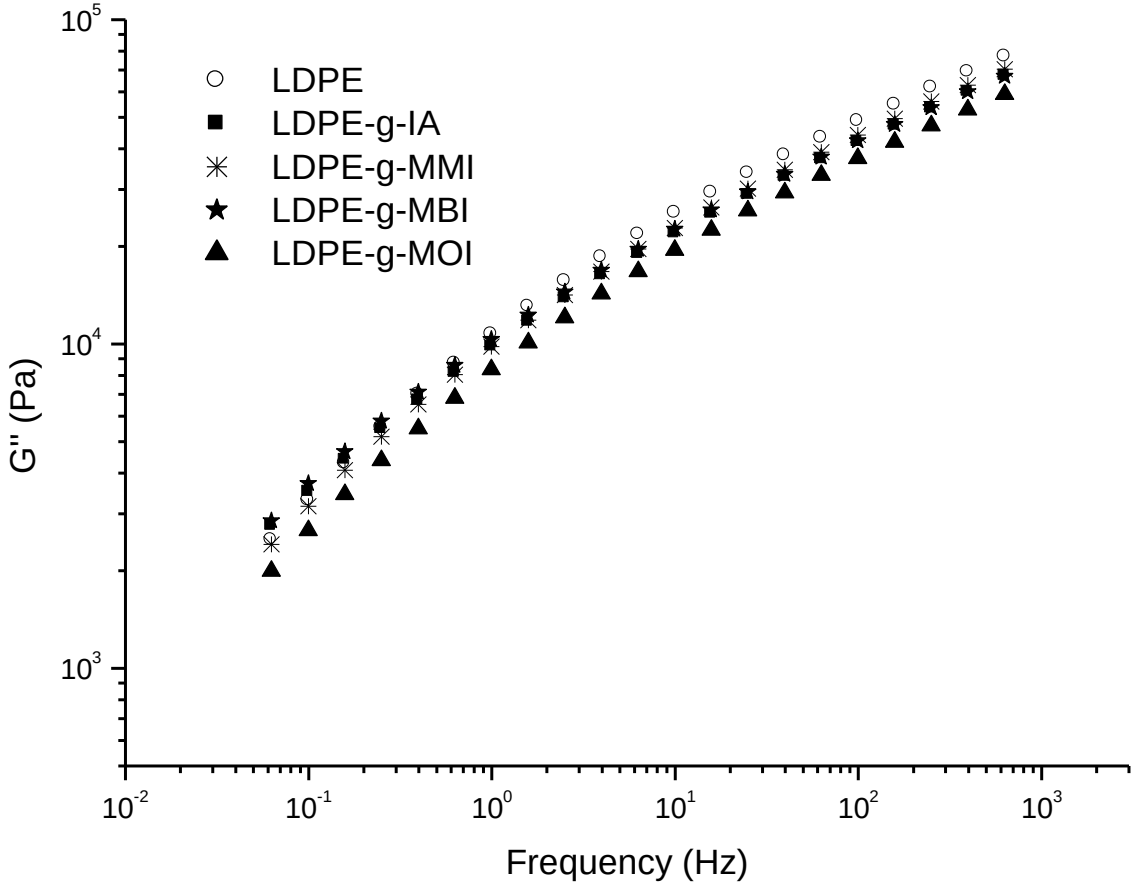

Fig 4.13 Loss Modulus (G'')- Frequency curve of LDPE and grafted LDPEs

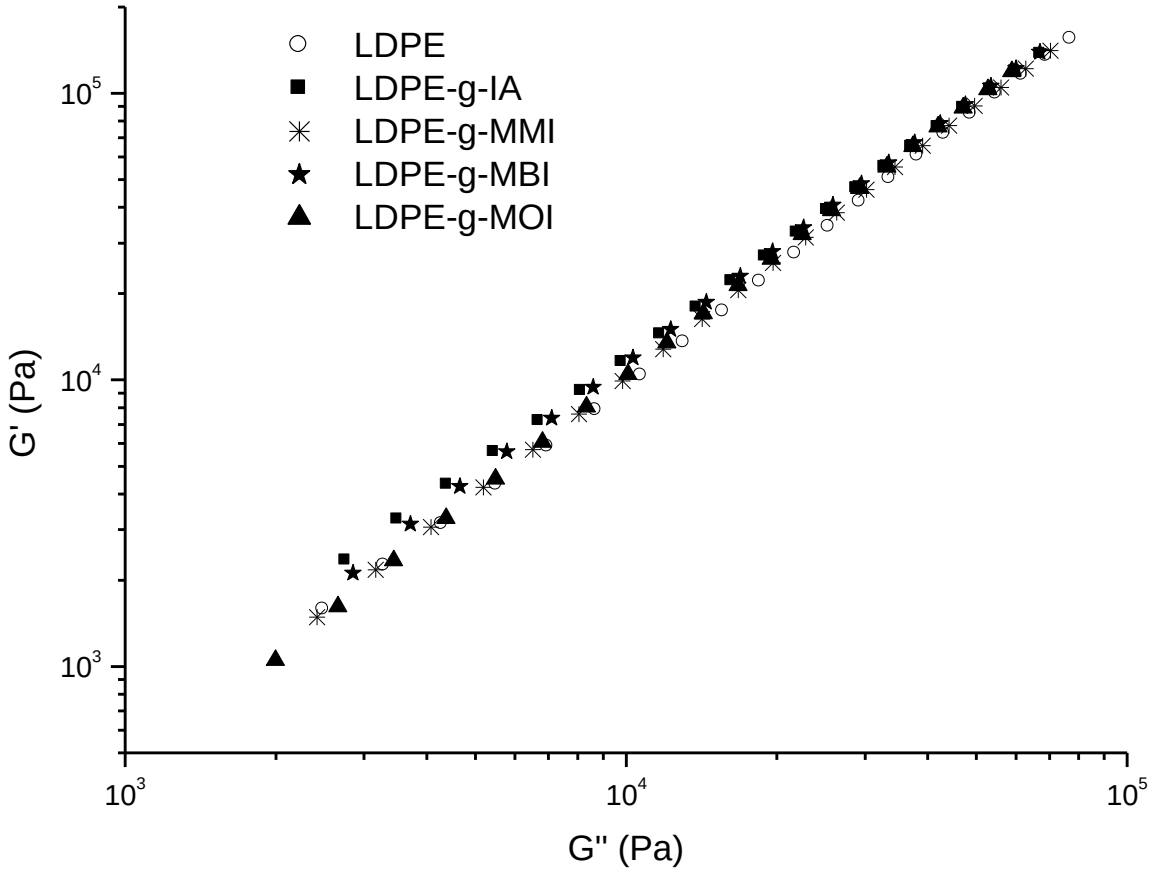

Fig 4.14 The log-log plot of Storage Modulus(G') and Loss Modulus (G'') of LDPE and grafted LDPEs

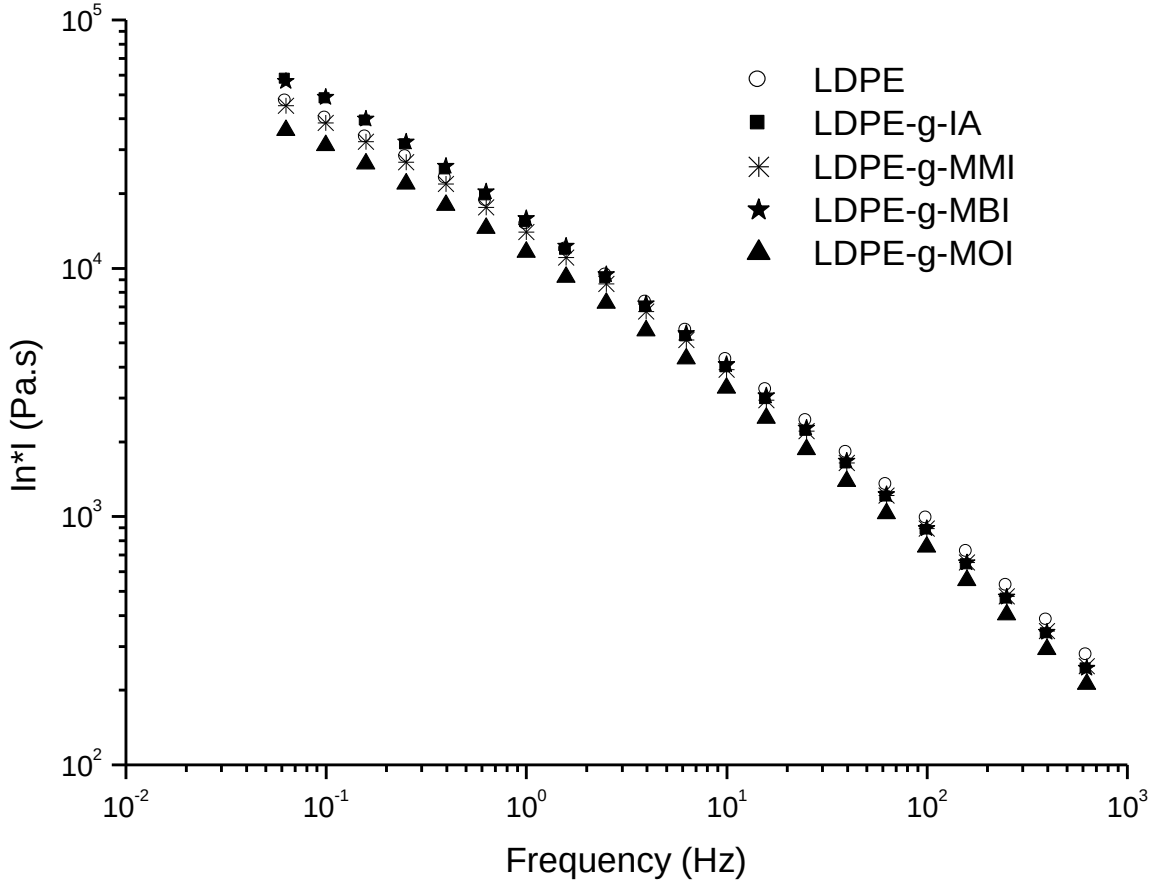

Fig 4.15. Complex viscosity-frequency curve of LDPE and grafted LDPEs

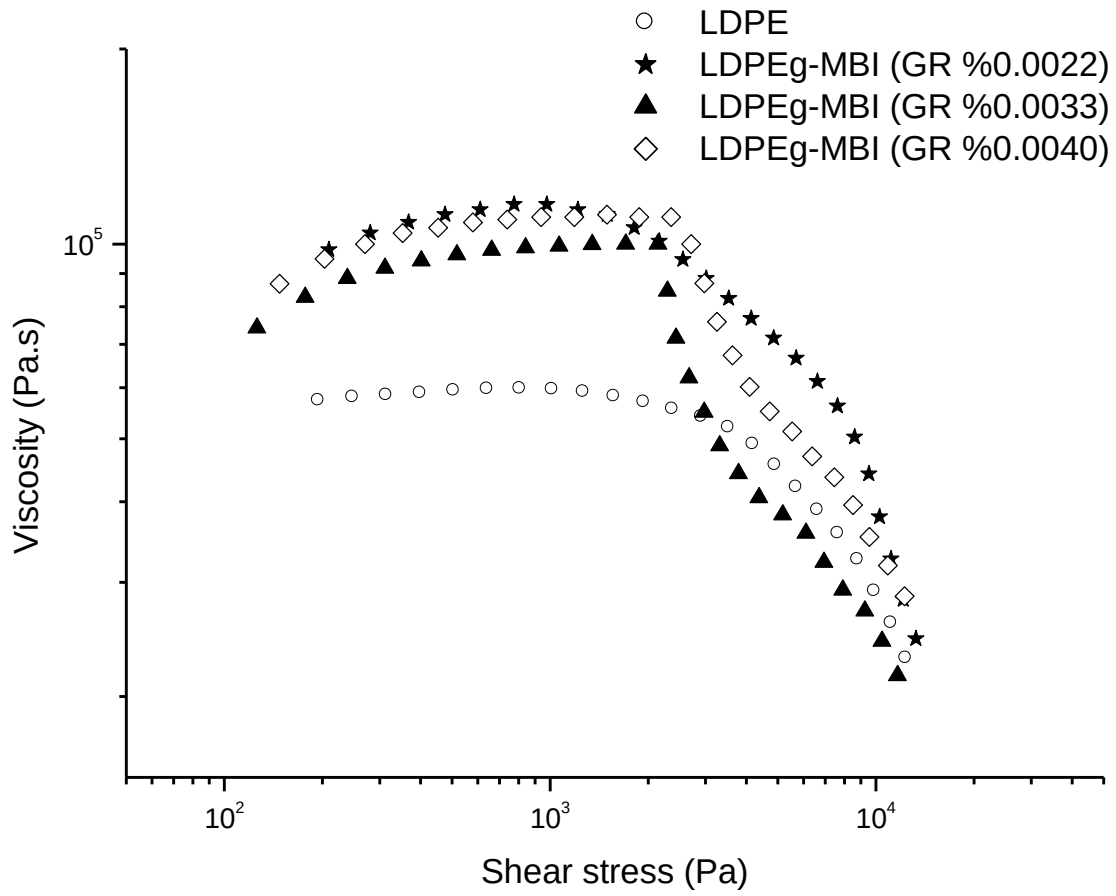

Fig 4.16. Viscosity-Shear stress curve of LDPE and LDPEs grafted with MBI

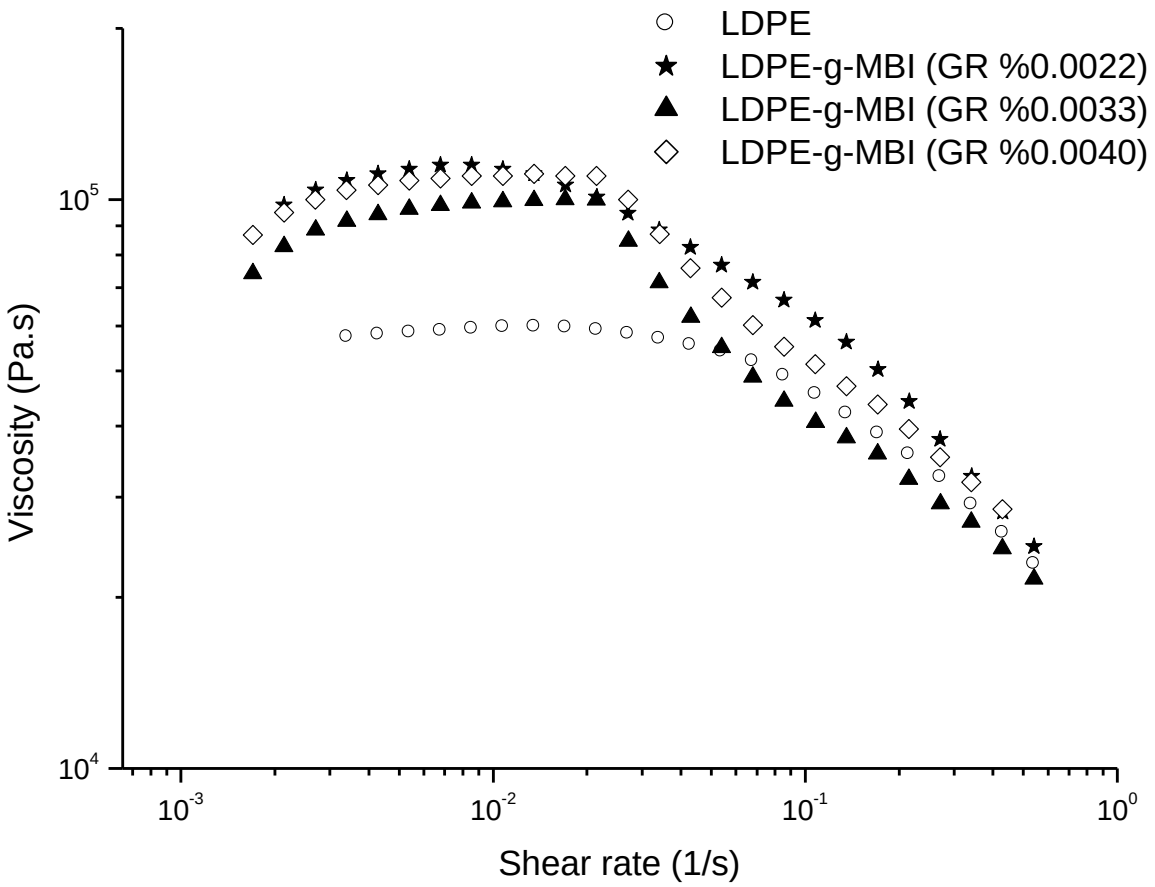

Fig 4.17. Viscosity-Shear rate curve of LDPE and LDPEs grafted with MBI

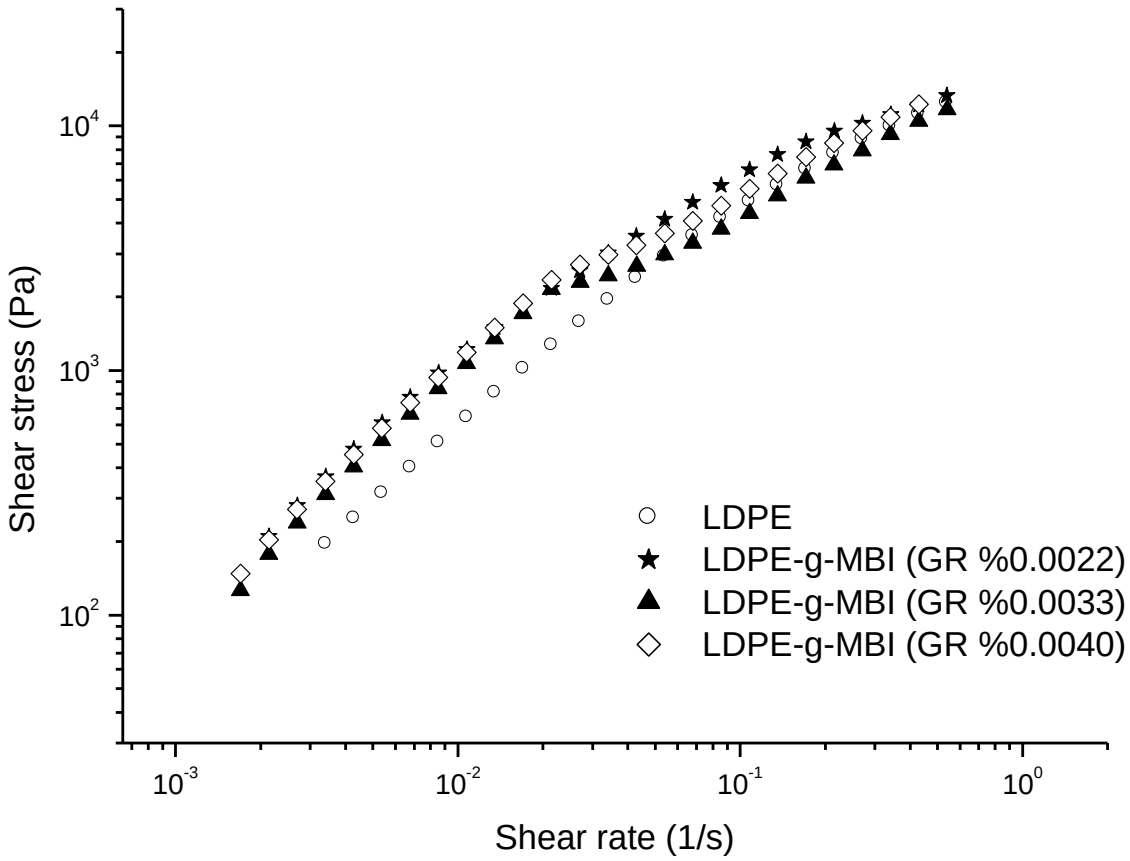

Fig 4.18. Shear stress-Shear rate curve of LDPE and LDPEs grafted with MBI

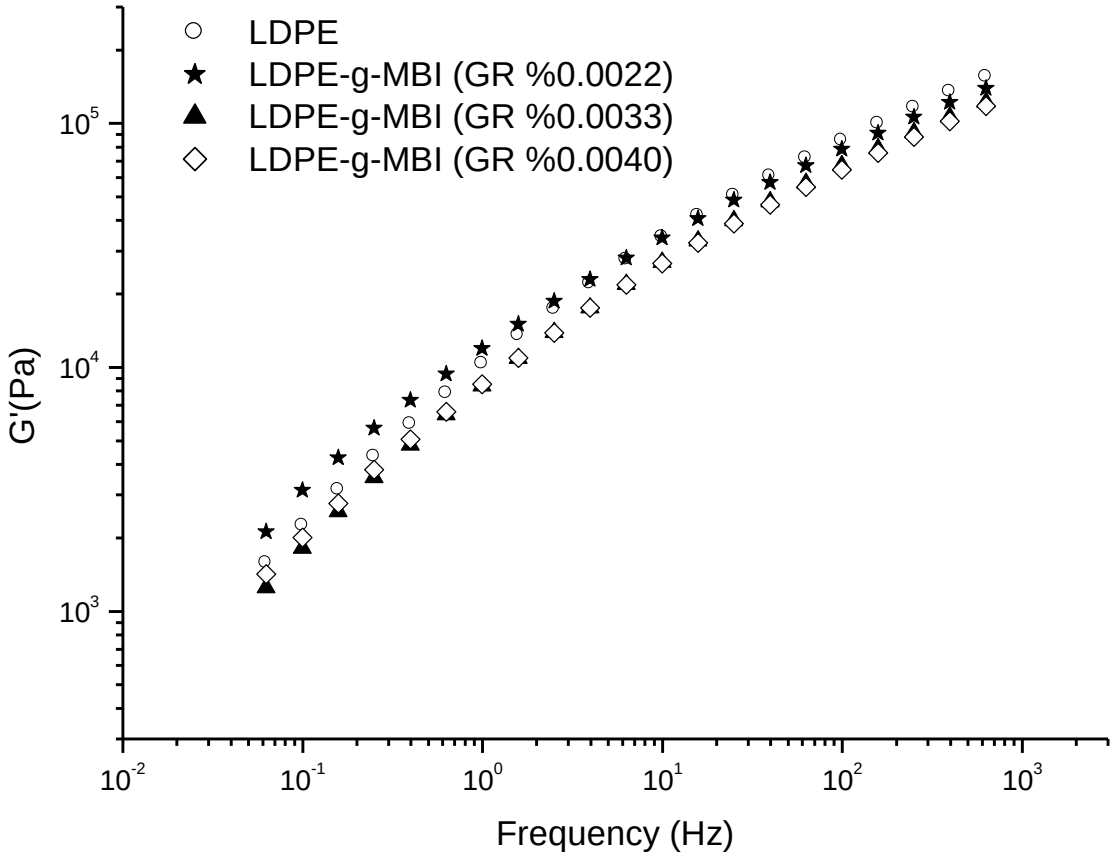

Fig 4.19. Storage Modulus (G')- Frequency curve of LDPE and LDPEs grafted with MBI

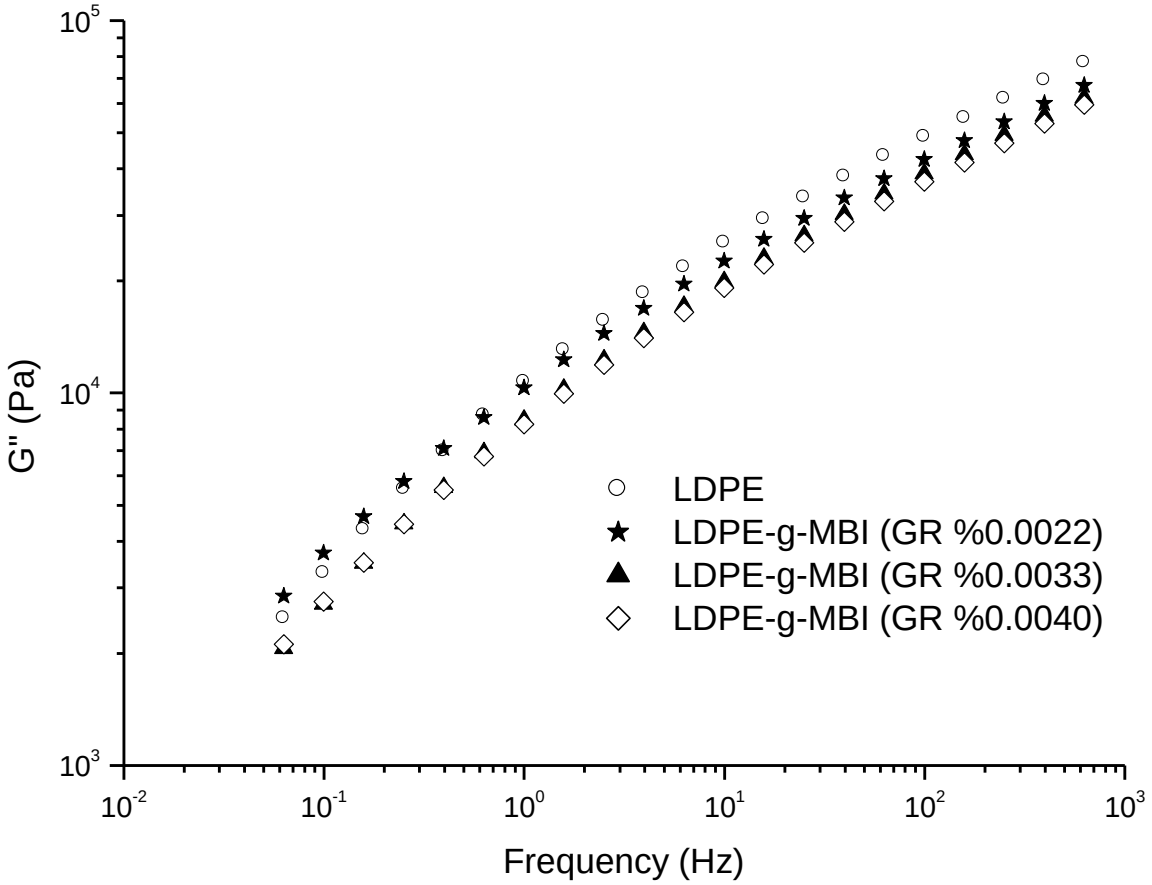

Fig 4.20 Loss Modulus (G'')- Frequency curve of LDPE and LDPEs grafted with MBI

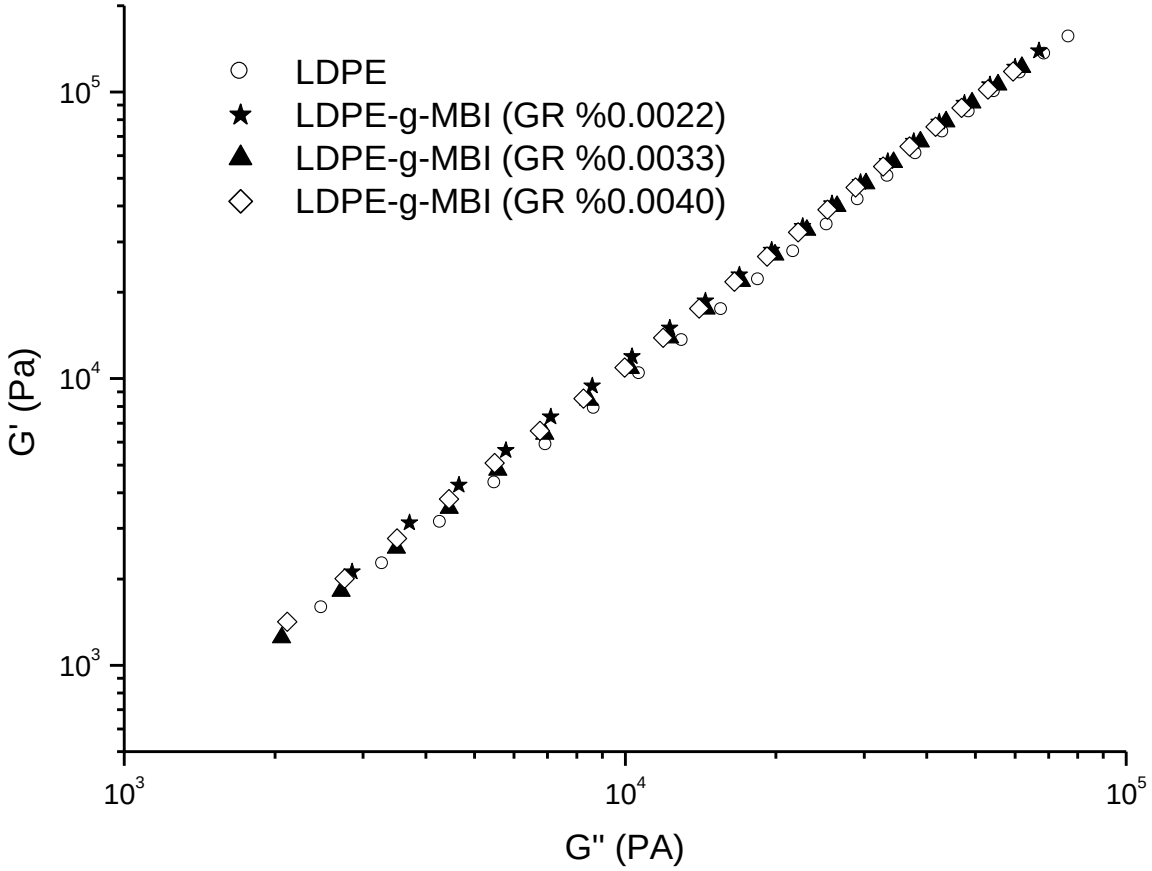

Fig 4.21 The log-log plot of Storage Modulus(G') and Loss Modulus (G'') of LDPE and LDPEs grafted with MBI

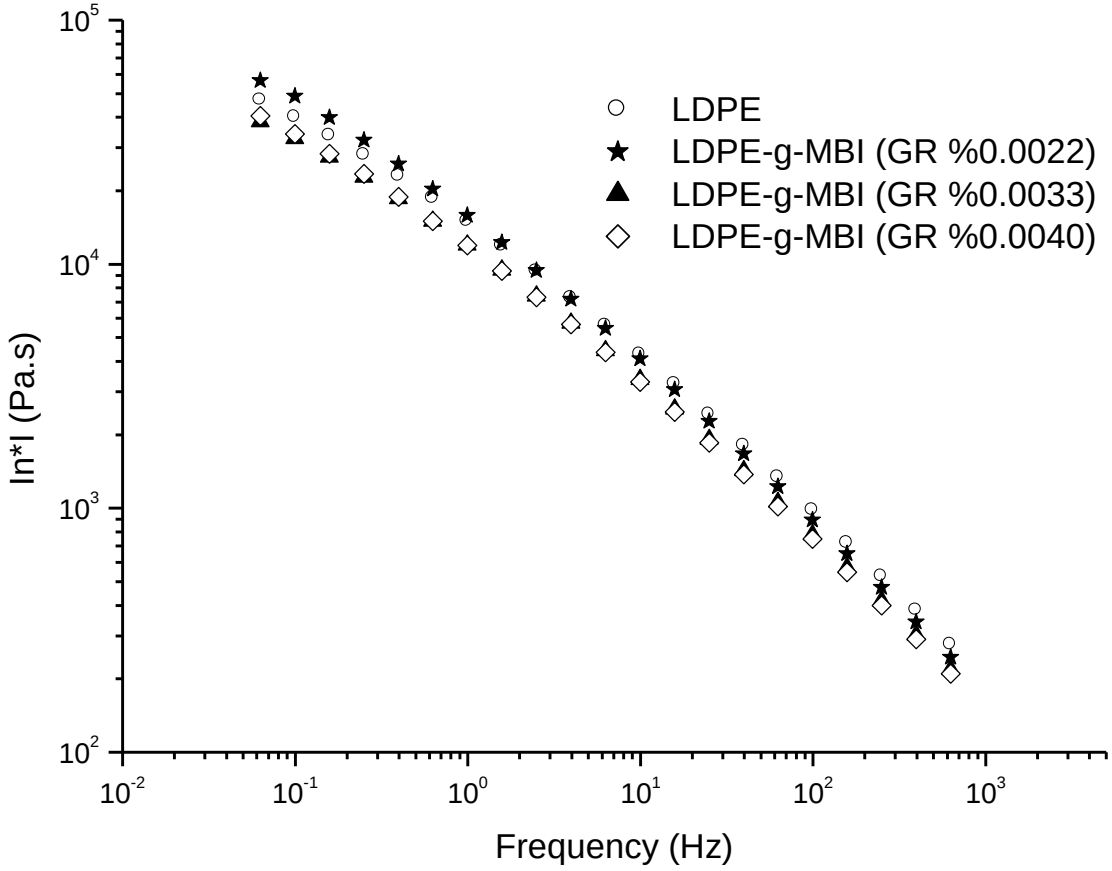

Fig 4.22. Complex viscosity-frequency curve of LDPE and LDPEs grafted with MBI

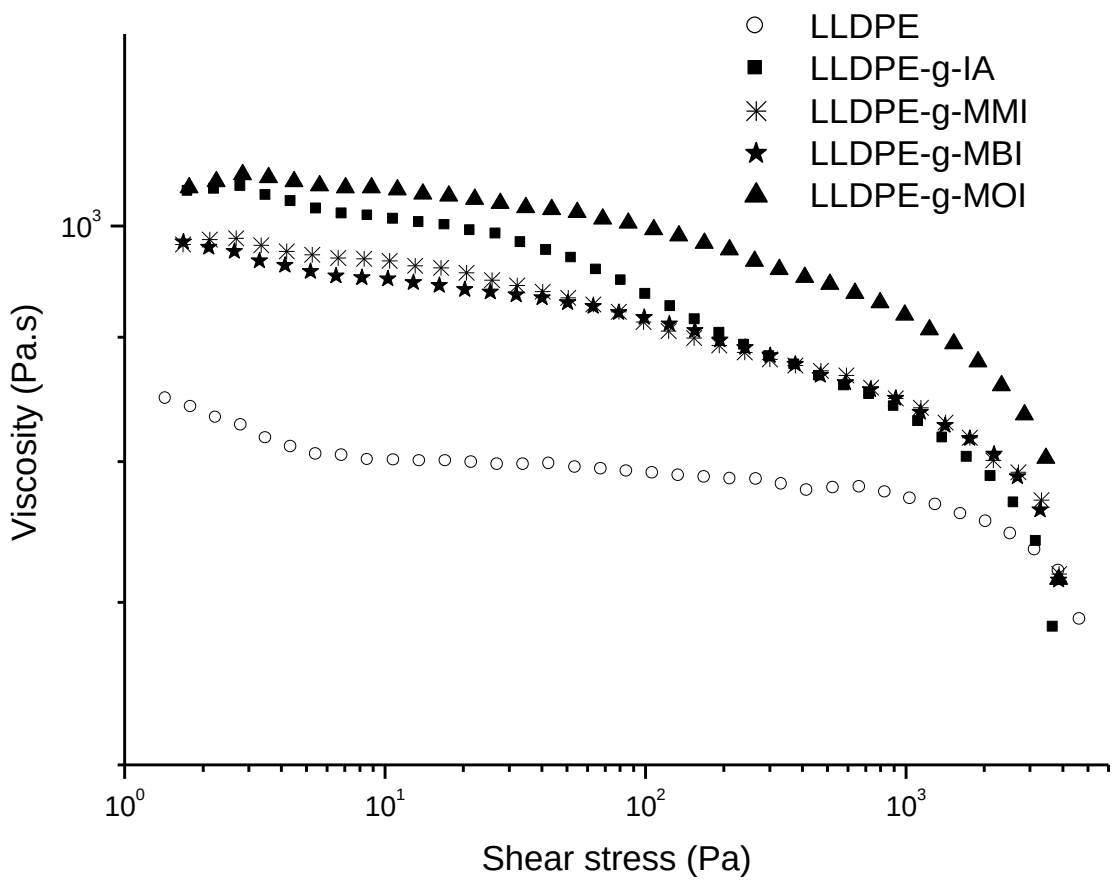

Fig 4.23. Viscosity-Shear stress curve of LLDPE and grafted LLDPEs

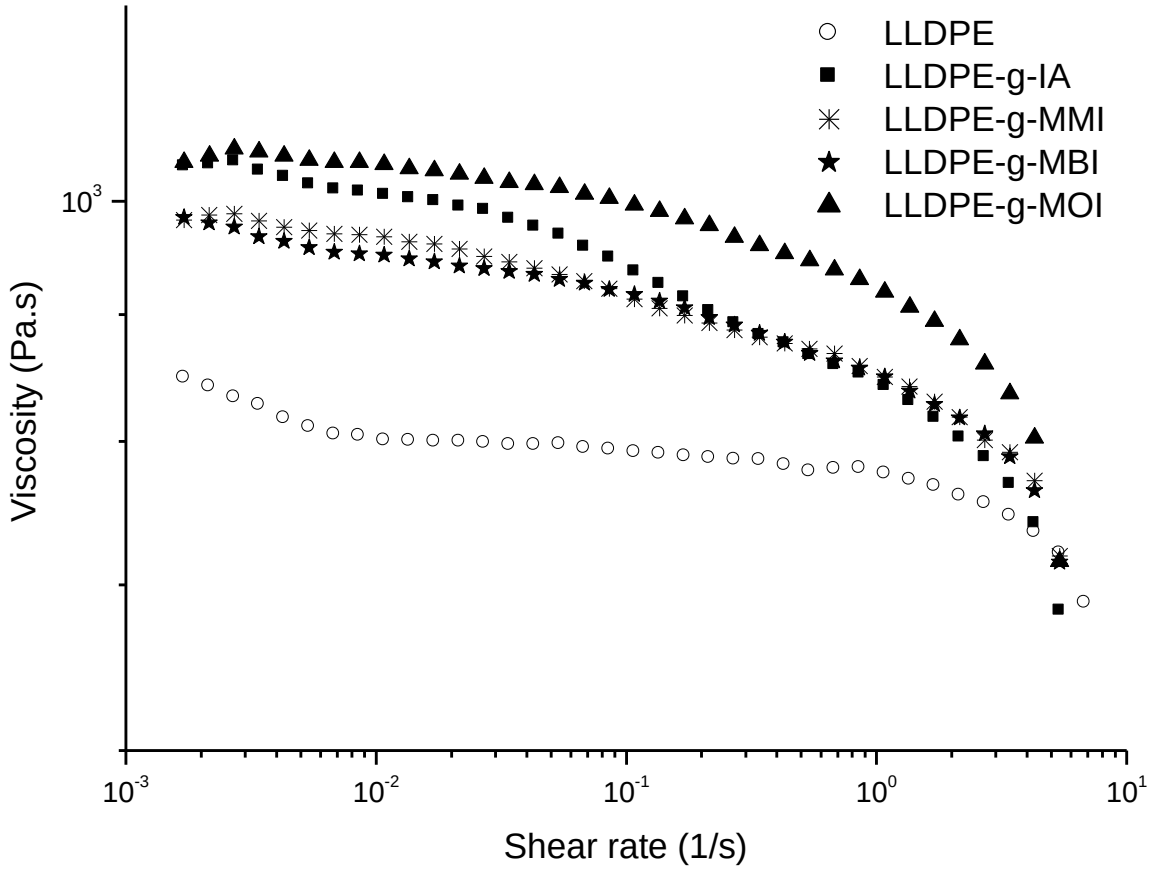

Fig 4.24. Viscosity-Shear rate curve of LLDPE and grafted LLDPEs

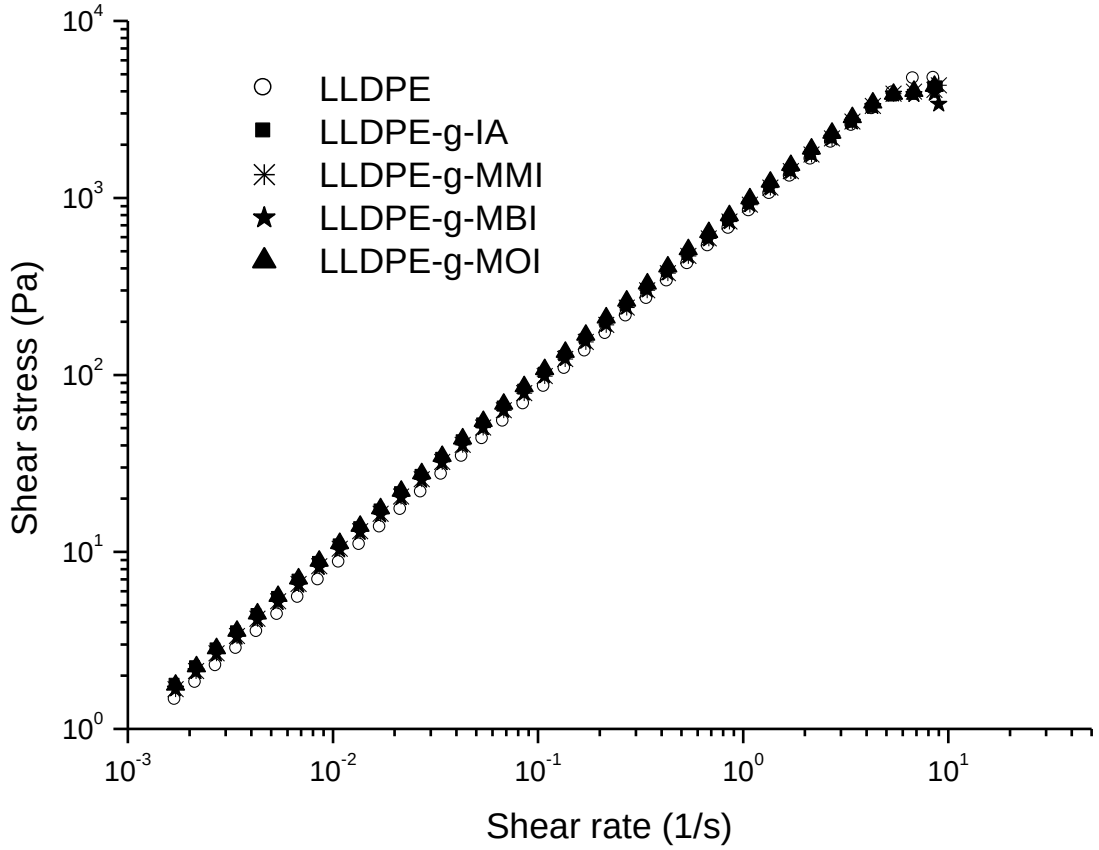

Fig 4.25. Shear Stress-Shear rate curve of LLDPE and grafted LLDPEs

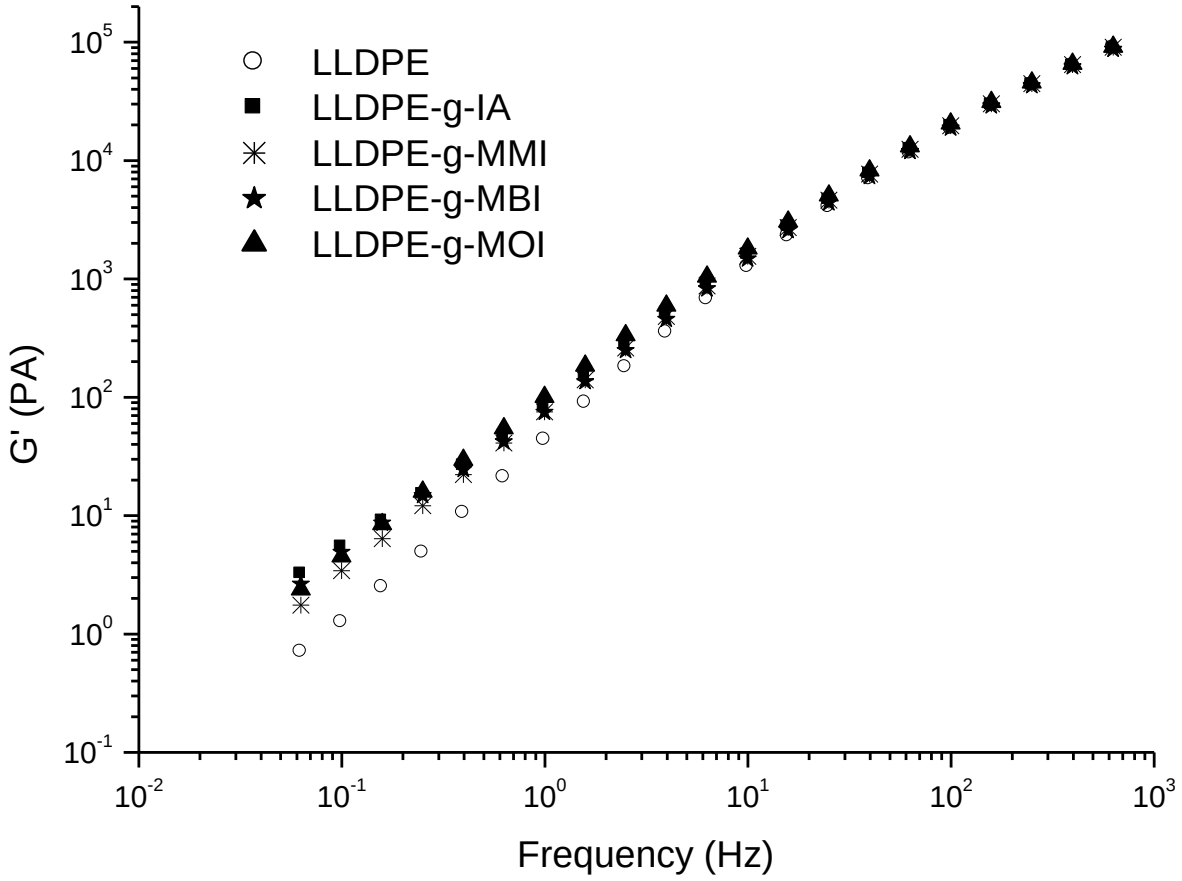

Fig 4.26. Storage Modulus (G')- Frequency curve of LLDPE and grafted LLDPEs

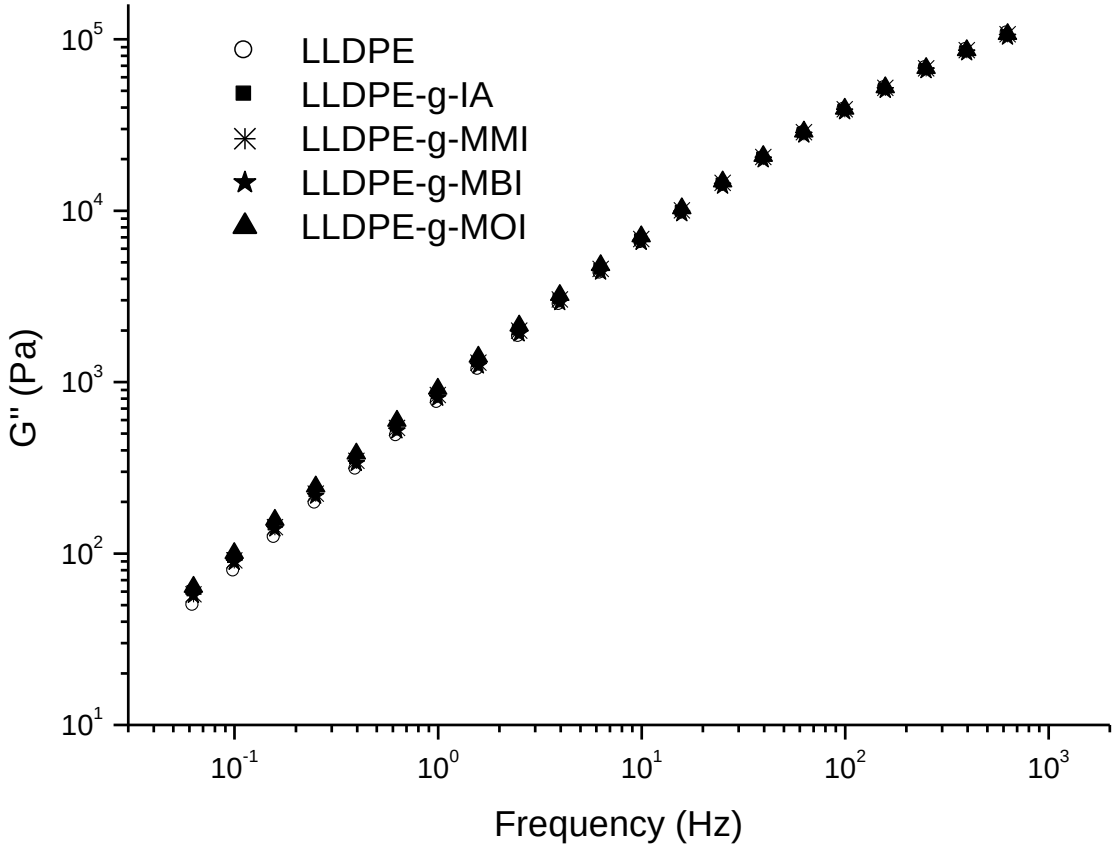

Fig 4.27. Loss Modulus (G'')- Frequency curve of LLDPE and grafted LLDPEs

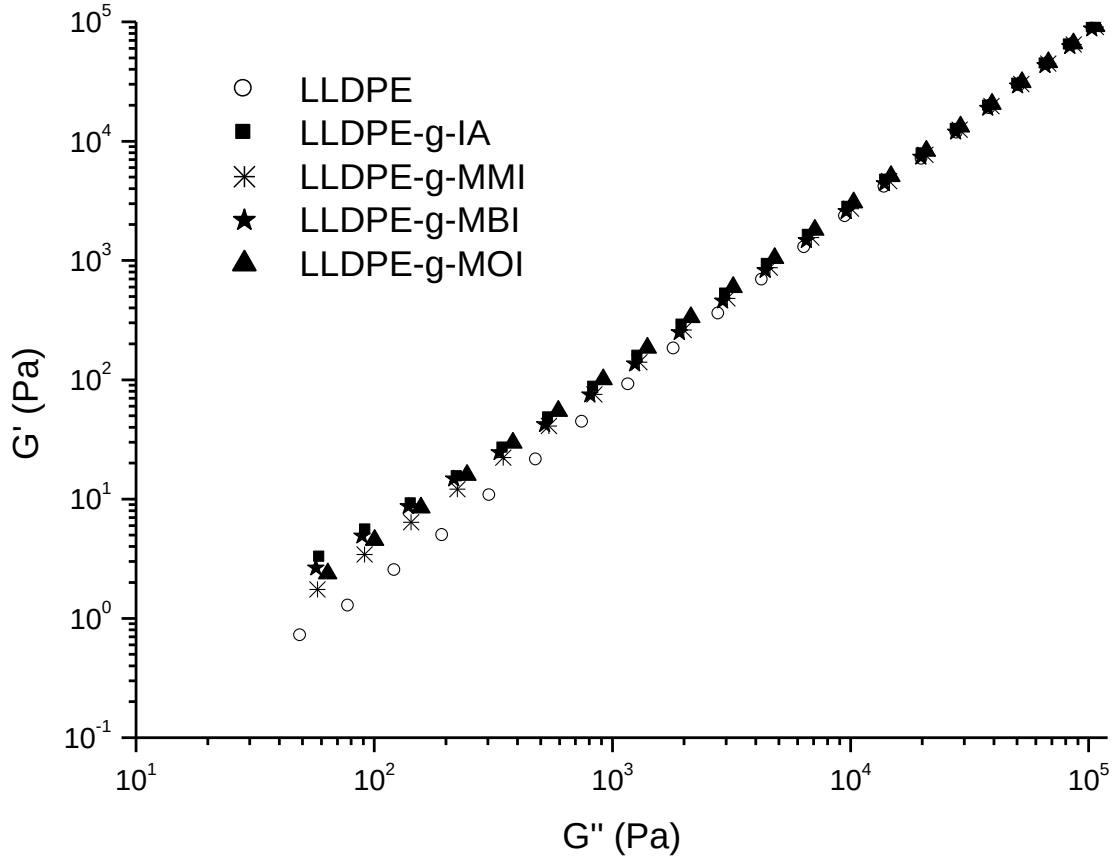

Fig 4.28. The log-log plot of Storage Modulus(G') and Loss Modulus (G'') of LLDPE and grafted LLDPEs

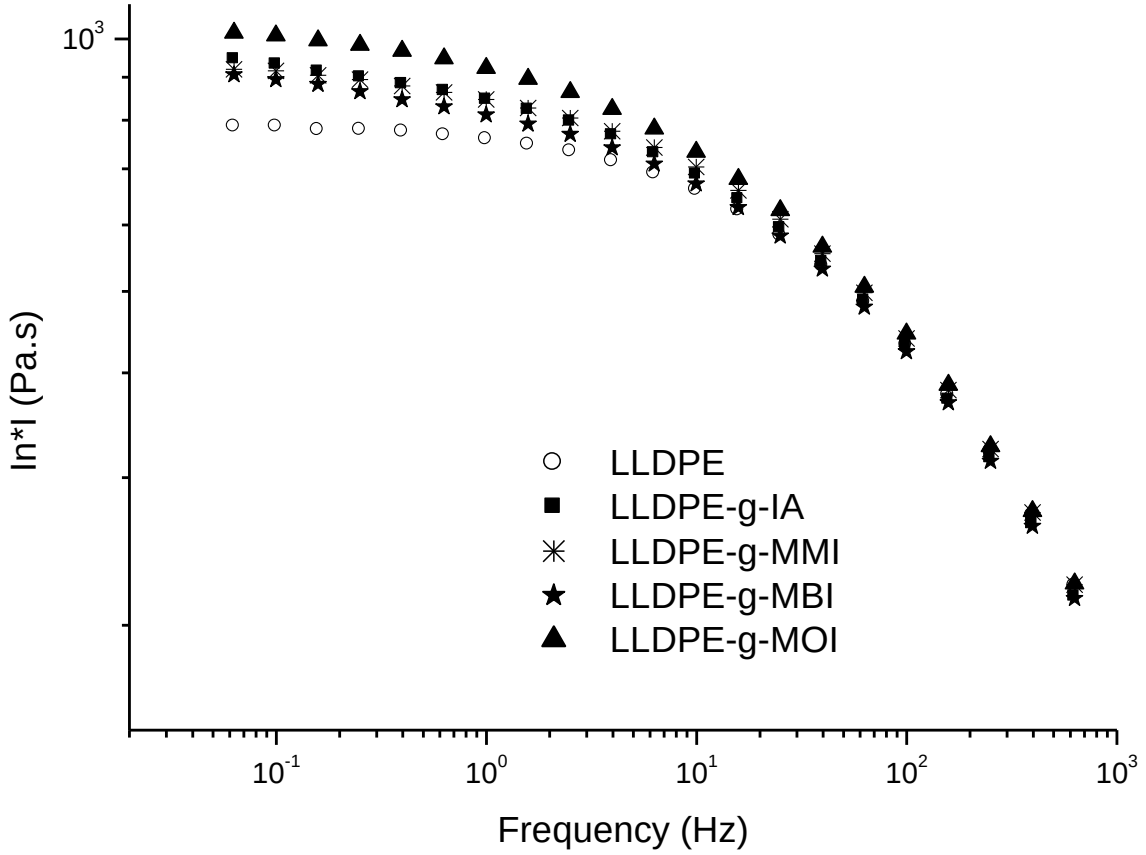

Fig 4.29. Complex viscosity-frequency curve of LLDPE and grafted LLDPEs

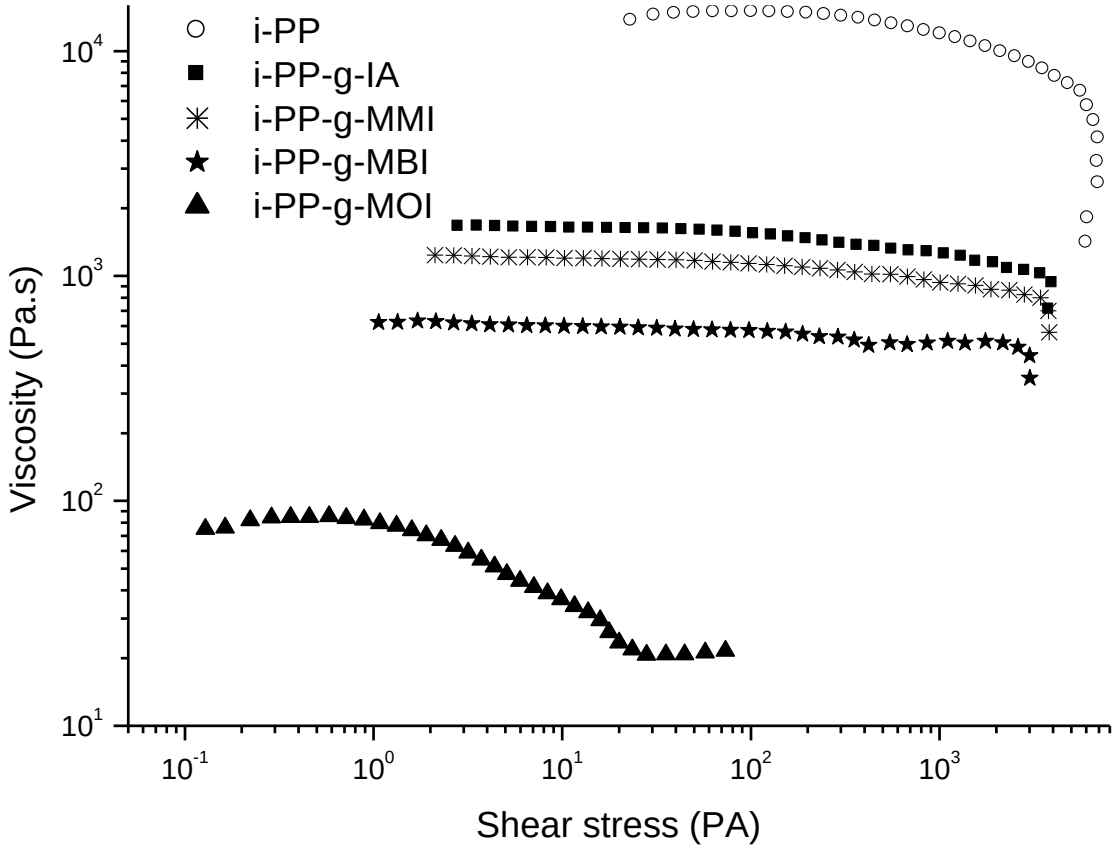

Fig 4.30 Viscosity-Shear stress curve of i-PP and grafted i-PPs

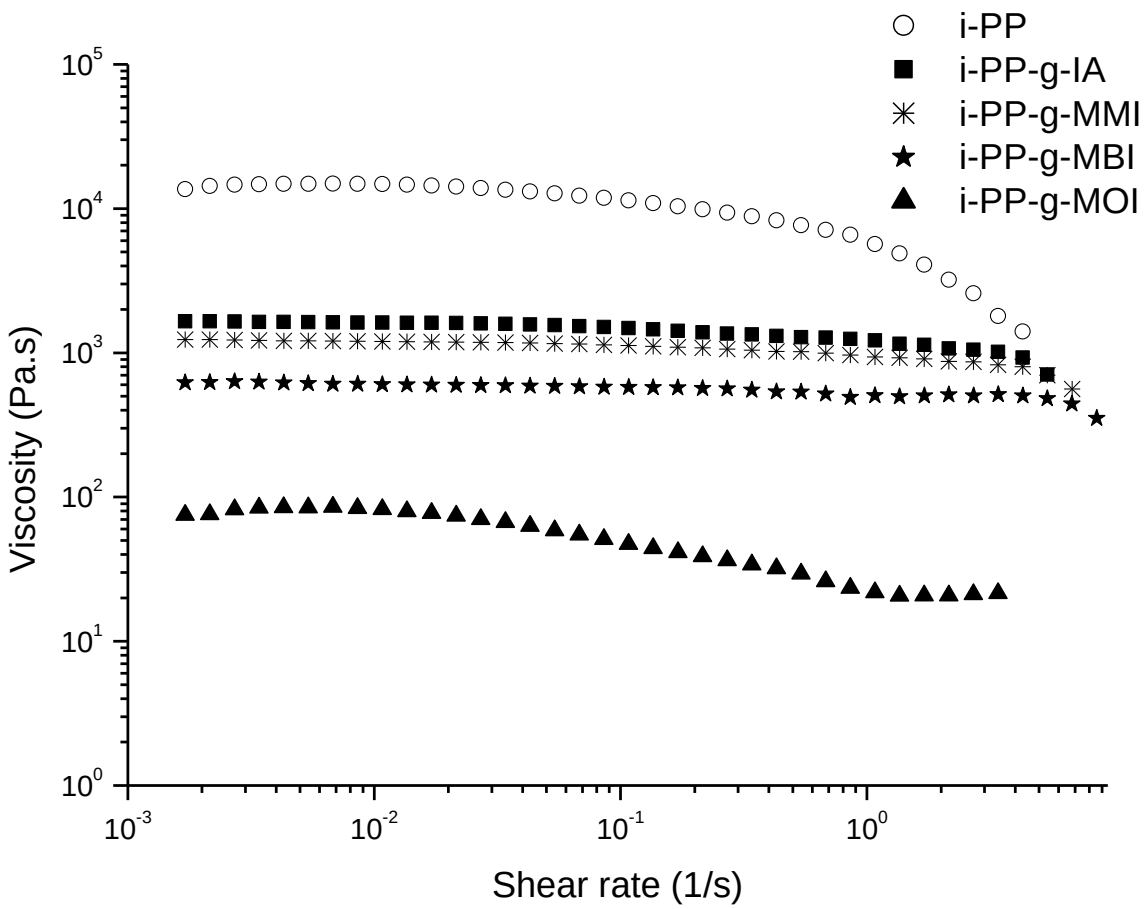

Fig 4.31 Viscosity-Shear rate curve of i-PP and grafted i-PPs

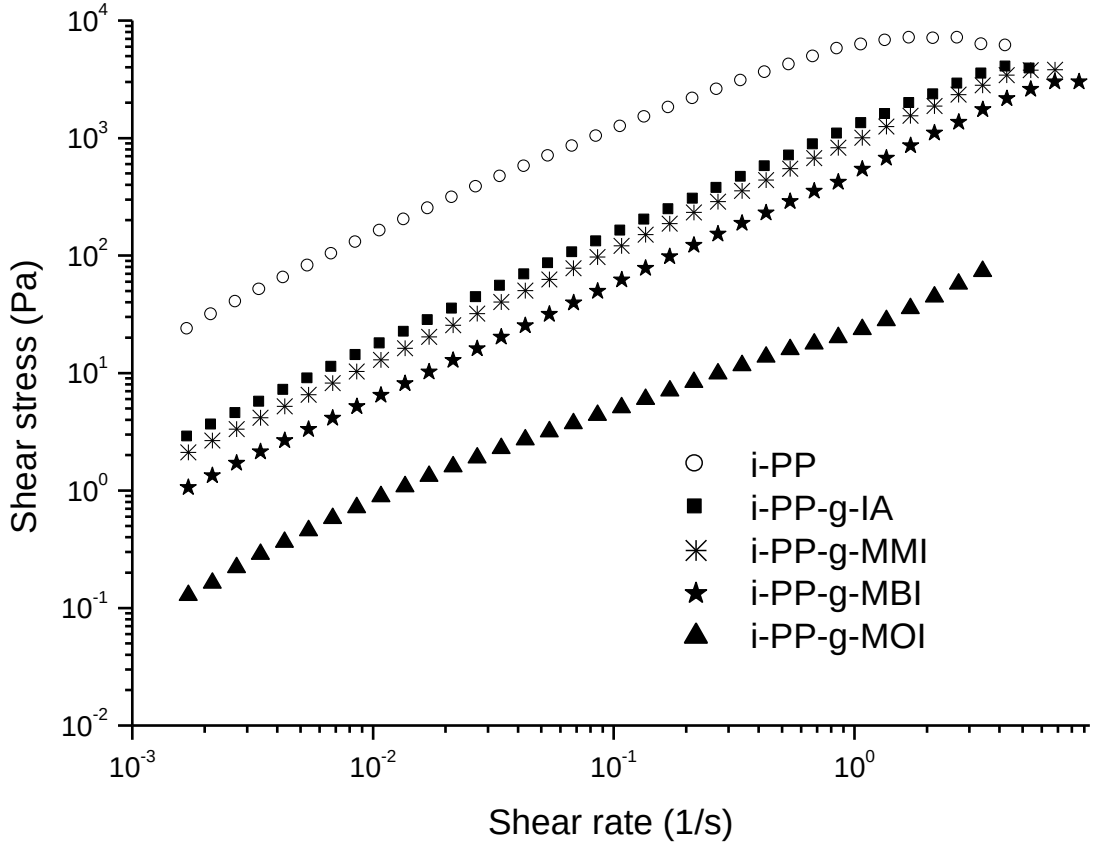

Fig 4.32 Shear Stress-Shear rate curve of i-PP and grafted i-PPs

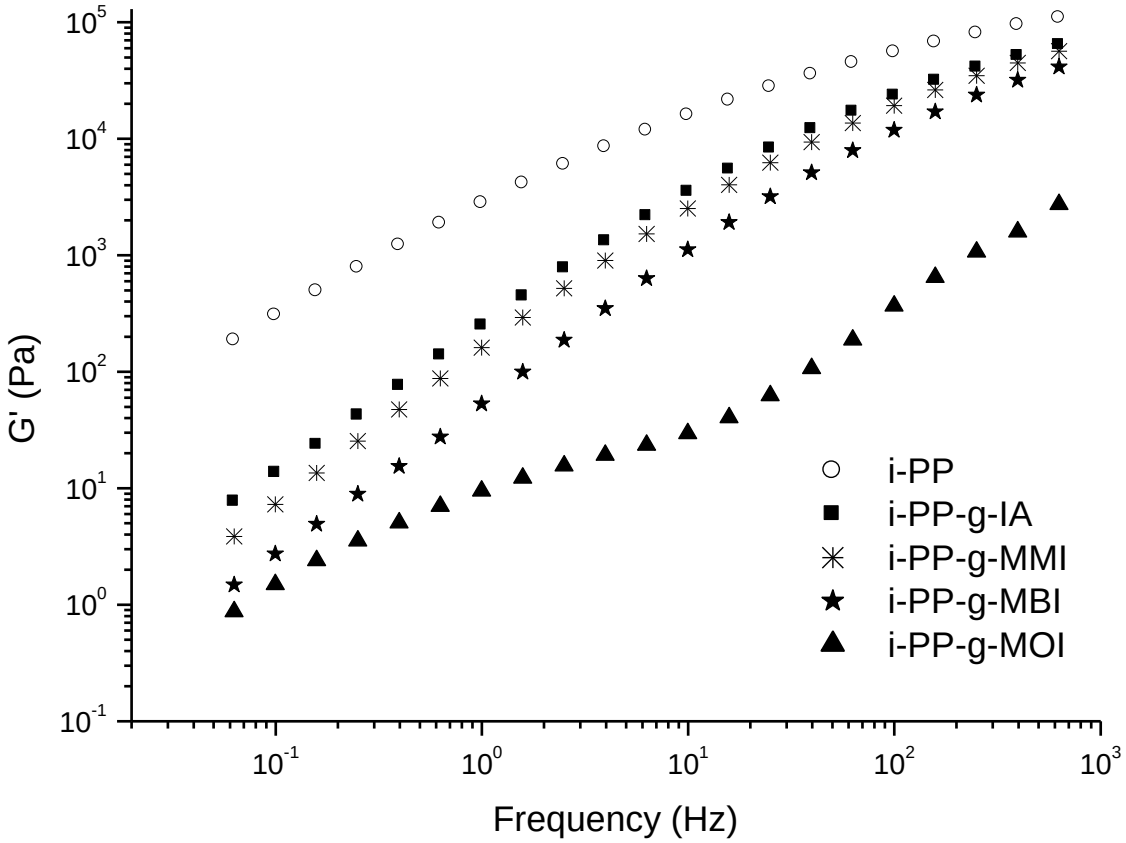

Fig 4.33 Storage Modulus (G')- Frequency curve of i-PP and grafted i-PPs

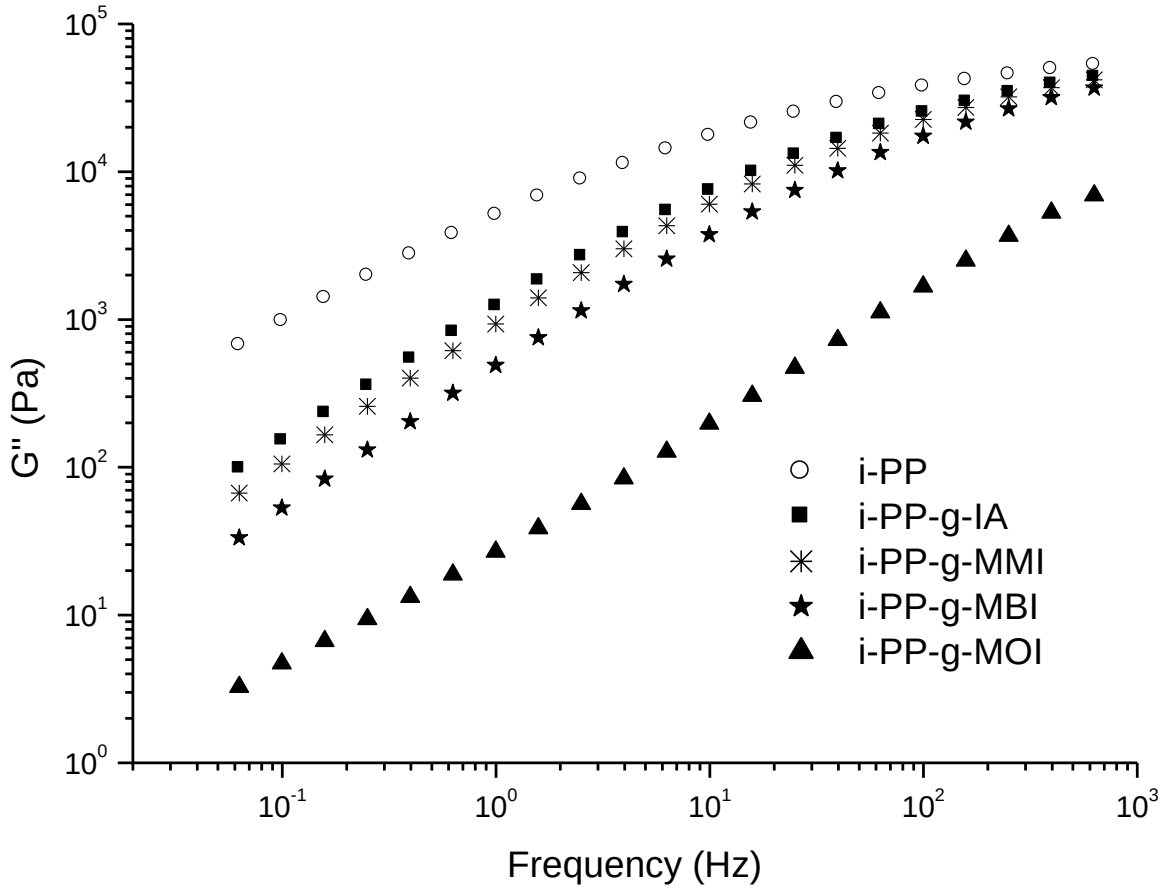

Fig 4.34 Loss Modulus (G'')- Frequency curve of i-PP and grafted i-PPs

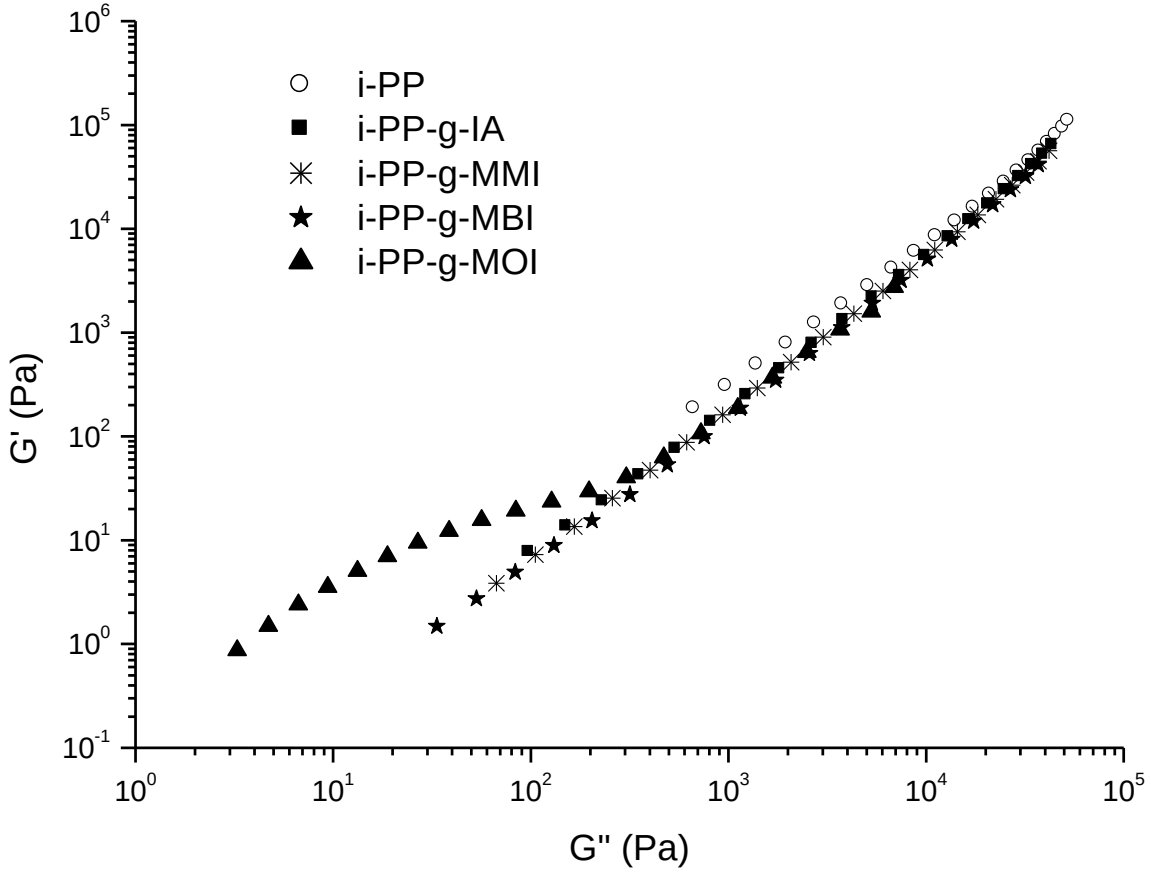

Fig 4.35 The log-log plot of Storage Modulus(G') and Loss Modulus (G'') of i-PP and grafted i-PPs

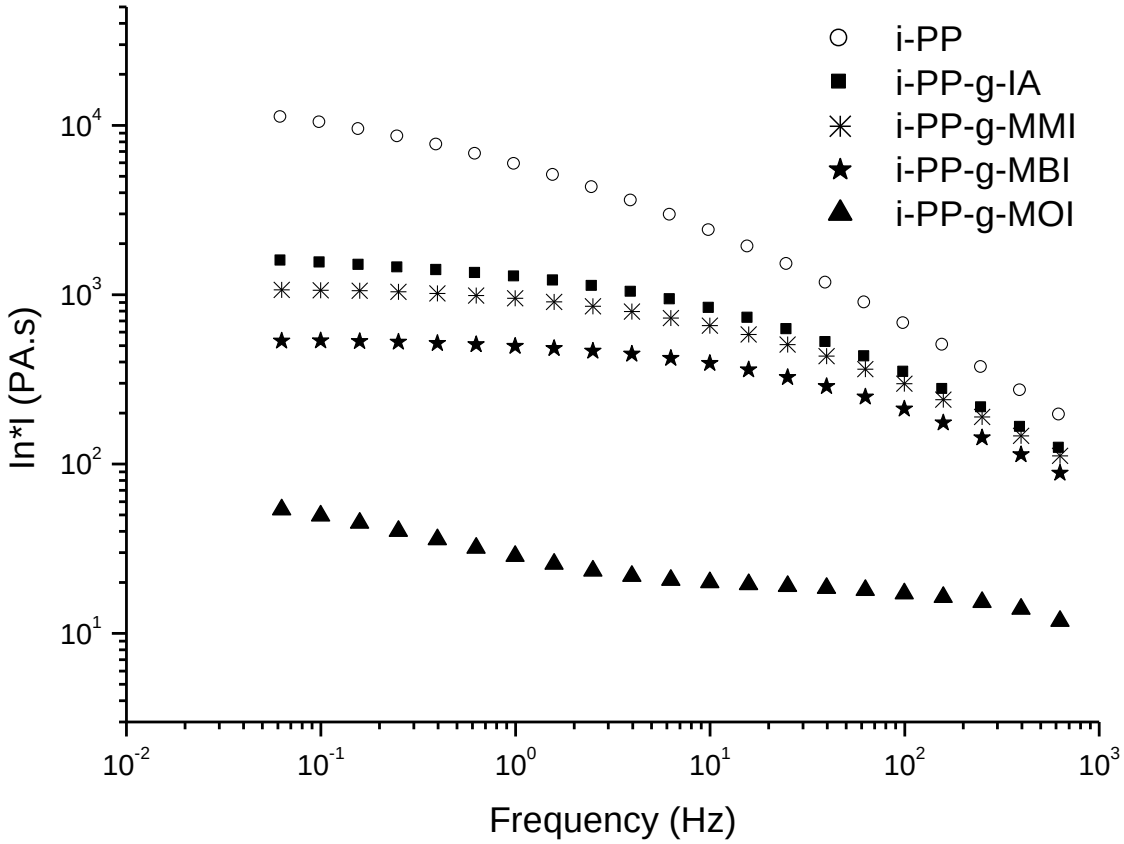

Fig 4.36. Complex viscosity-frequency curve of i-PP and grafted i-PPS

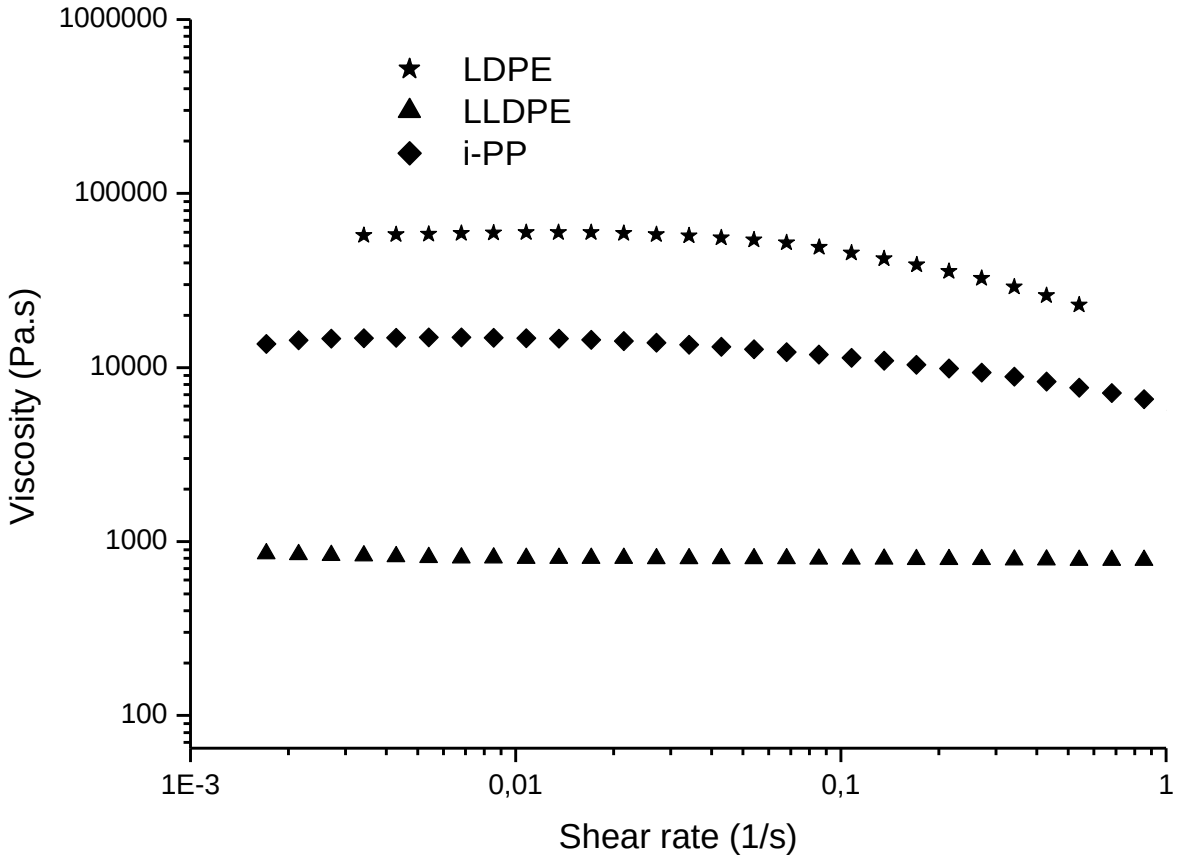

Fig 4.37 Viscosity-Shear rate curve of unmodified LDPE, LLDPE and i-PP

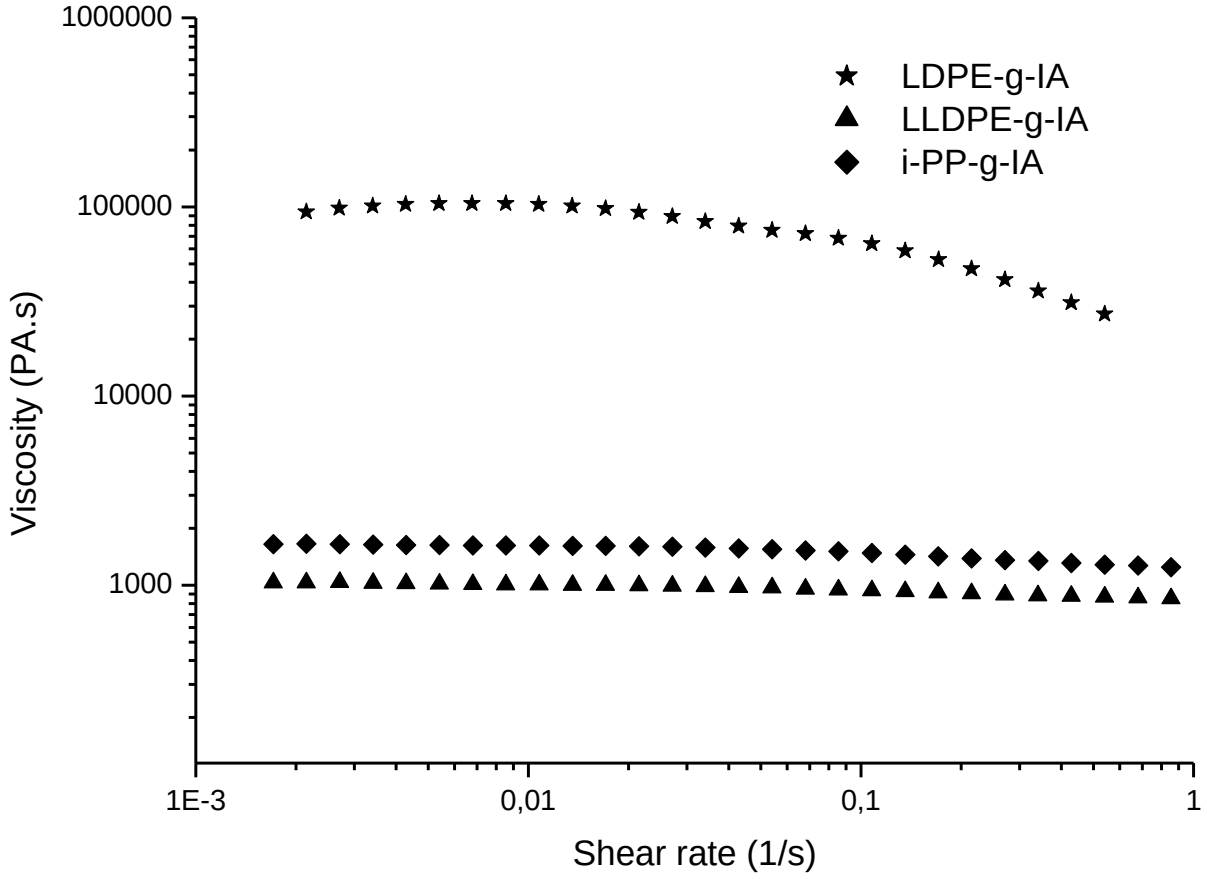

Fig 4.38 Viscosity-Shear rate curve of LDPE-g-IA, LLDPE-g-IA and i-PP-g-IA

BIOGRAPHY

She was born 1979 in Rize. She graduated from Bağcılar High School in 1996 and attempted to Chemical Engineering Department of Istanbul university in the same year.

In 2001 she graduated from university. She was accepted as a master student to Istanbul Technical University, Polymer Science and Technology Interdisciplinary graduate Programme and she is still completing her master education.